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THE MATHEMATICAL ANALYSIS OF LATTICE BOUNDARY VALUE PROBLEMS APPLIED TO MOLECULAR COLLISIONS WITH SURFACES

UNPUBLISHED PRELIMINARY DATA

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INTRODUCTION

The work reported in this paper can be considered in three distinct phases. First, the previously initiated study of the model for particle – surface collisions) proposed by Kinzer and Chambers[1] was completed. This included the calculation and analysis of the frequency spectrum excited in the solid and the calculation of thermal accommodation coefficients in the high-velocity limiting case.)Secondly, the equations of motion for the problem of the collision of a diatomic molecule with a crystal lattice in the one-dimensional approximation were solved and the high-velocity thermal accommodation coefficients were calculated and compared with the equivalent results for the monatomic collision problem. Finally, the mathematical techniques necessary for the treatment of boundary value problems involving repetitive structures such as crystal lattices were developed and applied to a variety of structures including simple three-dimensional lattices.

Author

PART I. THE MONATOMIC COLLISION

This study was initiated under Contract No. NAS8-2585 between the George C. Marshall Space Flight Center and the University of Alabama and preliminary results were reported in the form of an interim technical report. In that report criticism of prior work in the field was offered and justification for the model was presented in some detail. A summary of the results is given in section I. A.

Section I.A. Summary of Previous Results

The model consists of a semi-infinite chain of particles of mass m_1 interacting harmonically with their individual nearest neighbors through an elastic parameter $k_1 = m_1 \omega_1^2$. In addition, each particle is subject to a fixed harmonic interaction with elastic parameter $\overline{k} = 4m_1 \omega_1^2 \overline{\omega}^{-2}$ and to a linear, velocity dependent force with parameter $4m_1 \omega_1 K$. These last two terms represent the restorative and dissipative properties of the crystal bulk in terms of an essentially one dimensional model.

If we let a be the equilibrium separation of each pair of particles and $\phi_i(t)$ be the longitudinal displacement of the i^{TH} particle from equilibrium $i = 0, 1, 2, \cdots$, then the equations of motion become:

$$m_1 \ddot{\phi}_{n+1} = k_1 (\phi_{n+2} + \phi_n - 2\phi_{n+1}) - 4m_1 \omega_1^2 \bar{\omega}^2 \phi_{n+1} - 4m_1 \omega_1 K \dot{\phi}_{n+1}$$

$$n = 0, 1, 2, \cdots$$

$$m_1 \ddot{\phi}_o = k_1 (\phi_1 - \phi_o) - 4m_1 \omega_1^2 \bar{\omega}_1^2 \phi_o - 4m_1 \omega_1 K \dot{\phi}_o \qquad \text{(I.A. 1)}$$

The influence functions for this system of differential – difference equations can readily be found using the methods of PART III of this report. They are given by:

$$\psi_n = 2e^{-K\tau} \int_0^\tau J_o \left[(\bar{\omega}^2 - K^2)^{1/2} (\tau^2 - \sigma^2)^{1/2} \right] \frac{n J_n(\sigma)}{\sigma} \, d\sigma$$

$$\text{(I.A. 2)}$$

wherein τ is the reduced time, i.e., $\tau = 2\omega_1 t$, and $J_n(x)$ is the Bessel Function of order n.

Now consider an incident gas particle of mass m_o interacting harmonically with the end $(n = 0)$ particle of the lattice with an elastic parameter $k_o = m_o \omega_o^2$. Let the equilibrium separation of m_o and m_1 be a_o, and assume that the interaction ceases whenever the relative displacement of m_o and m_1 exceeds αa_o, where α is related to the binding energy ϵ by

$$\epsilon = \frac{1}{2} m_o \omega_o^2 \alpha^2 a_o^2 .$$

If we let $\xi(t)$ be the displacement of the incident particle from equilibrium, we can define the following:

$$\text{mass ratio} \; - - - - - - - - - - - - \; \mu = \frac{m_o}{m_1}$$

$$\text{ratio of elastic parameters} \; - - - - \; \beta = k_o / k_1$$

$$\text{relative displacement} \; - - - - - - \; u = \phi_o - \xi$$

and the equations of motion of the system become:

$$m_o \ddot{\xi} = k_o(\phi_o - \xi)$$

$$m_1 \ddot{\phi}_o = k_1(\phi_1 - \phi_o) + k_o(\xi - \phi_o) - 4m_1\omega_1^2 \bar{\omega}^2 \phi_o - 4m_1\omega_1 K \dot{\phi}_o$$

$$m_1 \ddot{\phi}_{n+1} = k_1(\phi_{n+2} + \phi_n - 2\phi_{n+1}) - 4m_1\omega_1^2 \bar{\omega}^2 \phi_{n+1} - 4m_1\omega_1 K \dot{\phi}_{n+1}$$

$$n = 0, 1, 2, \cdots .$$

(I.A. 3)

Assuming that the crystal is initially cold, the initial conditions are:

$$\phi_n(0) = \dot{\phi}_n(0) = 0 , \quad n = 0, 1, 2, \cdots$$

$$\xi(0) = -\alpha a_o , \quad \dot{\xi}(0) = 2\omega_1 \alpha a_o \gamma .$$

(I.A. 4)

Proceeding as before, these equations can be solved by the methods of PART III and the relative displacement $u(\tau)$ can be represented by a series of the influence functions for the lattice without the incident particle,

$$u(\tau) = \sum_{n=0}^{\infty} C_n \psi_n(\tau)$$

(I.A. 5)

where the C_n are functions of μ and β and can be determined recursively for any particular case.

The conditions for trapping of the incident particle on the surface can be obtained by assuming that the interaction begins with $u(0) = \alpha a_o$ and terminates for $\tau = \tau_e > 0$ when $u(\tau_c) = \alpha a_o$. A critical initial kinetic energy K_c can be defined such that $\bar{K}_c = \frac{K_c}{\epsilon} = \frac{4\mu}{\beta} \gamma_c^2$ where γ_c assumes a value such that $\dot{u}(\tau_c) = 0$ when $u(\tau_c) = \alpha a_o$. If $\bar{K}_c$ is plotted versus $z = \frac{1}{2}\sqrt{\mu\beta}$, for fixed μ and variable β, the effect of the parameters on the possibility of trapping may be studied. This feature of the model was thoroughly investigated in the previously mentioned report. Briefly, for a typical curve, the curve was roughly bell-shaped, with a more or less sharply peaked maximum indicating a resonance for particular choices of the parameters μ, β, K, and $\bar{\omega}$, and in general the efficiency of trapping was much higher than for models previously considered[2,3,4,5]. The effect of an increase in $\bar{\omega}$ was to mag-

nify the curve and displace the maximum to higher values of z , and the effect of increasing K was to reduce the height and increase the width of the resonant peak.

An expression for the vibrational frequency spectrum in the solid can be obtained by considering the energy flux through the lattice. The energy per unit time passing the first particle $(n = 0)$ in the lattice is given by $j(t) = m_o \omega_o^2 u \dot\phi_o$, and by resolving u and $\dot\phi_o$ into their Fourier components and considering the total flux of energy,

$$J = \int_0^\infty j(t)\, dt = \int_{-\infty}^\infty f(\omega)\, d\omega,$$

we can identify $f(\omega)$ as the frequency spectrum. In particular, we find

$$f(\omega) = \frac{\dfrac{8\beta\mu^2}{\pi\omega_1}\left[\epsilon\omega^2 + \dfrac{K_\epsilon\omega_o^2}{4\omega_1^2}\right] P_o \left[(P_o^2 + 1)^{1/2} + P_o\right]\left[-i\omega\right]}{\left\{-2\mu\omega^2\left[2P_o(\{P_o^2+1\}^{1/2}+P_o)+\beta\right]+\beta P_o(\{P_o^2+1\}^{1/2}+P_o)\right\}\left\{\begin{array}{c}\text{complex}\\\text{conjugate}\end{array}\right\}}$$

(I.A. 6)

$$P_o^2 = (K + i\omega)^2 + (\bar\omega^2 - K^2)$$

$$K_\epsilon = 2m_o\omega_1^2 \alpha^2 a_o^2 \gamma^2$$

Section I.B. The Frequency Spectrum

The developments in Section I.C. and Part III indicate that for realistic solids the dissipative parameter K is quite small. For this reason and for mathematical simplicity, we shall consider the frequency spectrum only in the case $K = 0$. The expression for $f(\omega)$ becomes

$$f(\omega) = \frac{\dfrac{8\beta\mu^2}{\pi\omega_1}\left[\epsilon\omega^2 + \dfrac{K_\epsilon\omega_o^2}{4\omega_1^2}\right]\left[\omega^4 - \omega^2\bar\omega^2\right]^{1/2}\left[1 - (\omega^2 - \bar\omega^2)\right]^{1/2}}{\left[\beta - 4\mu\omega^2\right]^2\left[\omega^2 - \bar\omega^2\right] + 4\mu\beta\omega^2\left[\beta - 4\mu\omega^2\right]\left[\omega^2 - \bar\omega^2\right] + 4\mu^2\beta^2\omega^4}$$

(I.B. 1)

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If we substitute $\omega_2^2 = \dfrac{\beta}{4\mu} = \dfrac{\omega_o^2}{4\omega_1^2}$, $\omega_m = 2\omega_1$, and $z = \dfrac{1}{2}\sqrt{\mu\beta}$,

we can write equation (I.B. 1) in the form:

$$\frac{\pi \omega_m f(\omega)}{4} = \frac{z\omega_2 \left[\epsilon \omega^2 + K_\epsilon \omega_2^2\right]\left[\omega^2(\omega^2 - \bar{\omega}^2)\right]^{1/2}\left[1 - (\omega^2 - \bar{\omega}^2)\right]^{1/2}}{\left[\omega_2^2 - \omega^2\right]^2\left[\omega^2 - \bar{\omega}^2\right] + 4z\omega_2\omega^2\left[\omega_2^2 - \omega^2\right]\left[\omega^2 - \bar{\omega}^2\right] + 4z^2\omega_2^2\omega^4}$$

(I.B. 2)

and in this form the equation was programmed for the IBM - 7090 computer of the Marshall Space Flight Center. Curves were calculated for various values of the parameters $\bar{\omega}$, ω_2 and z. It is interesting to note that in general ω is confined to the range

$$\bar{\omega}^2 \leq \omega^2 \leq 1 + \bar{\omega}^2$$

which means that the lattice behaves as a band-pass filter, i.e., only those frequencies within this range are transmitted by the lattice without attenuation. Because of this behavior, values of ω_2 were selected which, for each choice of $\bar{\omega}$, fell below, within, and above the range of ω . Because of the particular dependence of $f(\omega)$ on ϵ and K_ϵ , it was convenient to plot separately the terms proportional to these two quantities.

Figure 1. shows the dependence of the binding energy term on the parameter $\bar{\omega}$. In each case z was held constant and a value of ω_2 was chosen which fell approximately in the center of the allowed range of ω . Figure 2. indicates the dependence of the kinetic energy term on $\bar{\omega}$. Again, in each case z was held constant and ω_2 was chosen in the middle of the allowed range of ω . It is clearly seen that the effect of increasing $\bar{\omega}$ is to reduce the total amount of energy transferred to the lattice, which is represented by the area under the curve, without drastically altering the relative distribution of frequencies. This can be interpreted physically as a stiffening of the lattice in terms of its response to the collision of the incident particle.

Figure 3. exhibits the dependence of the kinetic energy term on the parameter ω_2. The binding energy term has qualitatively the same behavior and, since the kinetic

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energy term will be the dominant one in an energetic collision or the weak binding case, we confine our attention to the kinetic energy term. For ω_2 in the center of the allowed frequency band the distribution is roughly symmetric. When ω_2 is below the lowest allowed frequency band the distribution is roughly symmetric. When ω_2 is below the lowest allowed frequency the distribution is modified by a shift to a relatively larger number of higher allowed frequencies, while if ω_2 is above the highest allowed frequency the distribution is shifted to a relatively larger number of the lower allowed frequencies. The respective shifts are accompanied by a reduction in the area under the curve, i.e., by a reduced transfer of energy from the incident particle to the lattice. This is the same behavior which is more clearly exhibited by a study of the trapping curves referred to in Section I.A. It is apparent that ω_2 is a measure of the degree to which the properties of the incident gas particle match those of the solid.

Figure 4. illustrates the dependence of the kinetic energy term on the parameter z. An increase in z generally results in a decrease in the area under the curve, and hence the energy transferred. That this is physically reasonable can be seen from the fact that, to a first approximation, the effective duration of the collision is given by $\dfrac{1}{\omega_o z}$, thus the time available for the transfer of energy is less for large z. This effect is also apparent from a study of the trapping curves.

It is difficult to estimate just how good an approximation this frequency spectrum is to the actual frequency spectrum of a true three dimensional lattice, however, it is felt that the qualitative features should be similar. Verification must await the complete analysis of the three dimensional models.

Section I.C. Accommodation Coefficients

The effect of the stiffness and dissipation parameters on the energy transfer to the lattice from the incident gas particle can also be evaluated qualitatively by a study of the accommodation coefficient which is defined by the energy ratio

$$a.c. = \frac{K_i - K_f}{K_i}$$

(I.C. 1)

Where K_i is the kinetic energy of the gas particle before the collision and K_f is the kinetic energy after the collision. We have assumed the initial temperature of the surface to be sufficiently small so as to be negligible with respect to the effective temperature of the gas particle.

Since

$$a.c. = 1 - \frac{K_f}{K_i} = 1 - \left[\frac{\dot{\xi}(\tau_c)}{\dot{\xi}(0)} \right]^2 \qquad \text{(I.C. 2)}$$

where τ_c is the reduced time corresponding to the end of the collision, the velocity of the gas particle as a function of time can be found by integrating the equation

$$\ddot{\xi}(\tau) = \omega_o^2 (\phi_o - \xi) = \omega_o^2 u(\tau) \qquad \text{(I.A. 3)}$$

with respect to time. We have

$$\frac{d^2 \xi(\tau)}{d\tau^2} = \frac{1}{4\omega_1^2} \frac{d^2 \xi}{dt^2} = \frac{\omega_o^2}{4\omega_1^2} u(\tau)$$

$$\frac{d\xi}{d\tau} = \xi'(\tau) = \xi'(0) + \frac{\omega_o^2}{4\omega_1^2} \int_0^\tau u(s)\, ds$$

Since

$$\frac{\omega_o^2}{\omega_1^2} = \frac{\beta}{\mu} \quad \text{and we can write}$$

$$u(\tau) = u(0)\, \frac{df(\tau)}{d\tau} + u'(0)\, f(\tau)$$

We have

$$\frac{\xi'(\tau)}{\xi'(0)} = 1 + \frac{\beta}{4\mu\, \xi'(0)} \int_0^\tau \left[u(0)\, \frac{df(s)}{ds} + u'(0)\, f(s) \right] ds$$

Now by choosing $\alpha = 0$, we have $u(0) = 0$ and limit ourselves to the case of a purely repulsive potential. This also represents the high initial velocity (temperature) case in which the attractive part of the potential plays a negligible role. Because of the assumption of a cold surface

$$u'(0) = \phi'(0) - \xi'(0) = -\xi'(0)$$

and so we obtain

$$\frac{\dot{\xi}(\tau)}{\dot{\xi}(0)} = \frac{\xi'(\tau)}{\xi'(0)} = 1 - \frac{\beta}{4\mu} \int_0^\tau f(s)\, ds \tag{I.C. 4}$$

Then the accommodation coefficient is given by

$$a.c. = 1 - \left[1 - \frac{\beta}{4\mu} \int_0^{\tau_c} f(s)\, ds \right]^2 . \tag{I.C. 5}$$

τ_c in this relation is the reduced time corresponding to the first zero of the integral for nonzero time.

Referring to Figures 5. and 6. for $\mu = 1$ and $\mu = 1/2$, respectively, we see that the effect of increasing the stiffness parameter $\bar{\omega}$ is to shift the accommodation coefficient curve to larger values of β, i.e., the rigidity of the crystal lattice bond-rotational motion reduces the transfer of energy in the weak binding energy case. For $\beta > 3$, however, there is very little effect observed. In Figures 7. and 8. we see the result of an increase in the parameter K which governs the ability of the crystal to extract energy from the primary chain. The "knee" of the a.c. curve is not appreciably displaced but the height of the curve is drastically reduced until one reaches the critical case $\bar{\omega} = 1$, $K = 1$ for which the motion of the lattice particles is exponentially damped. This effect implies that the end lattice particle becomes more difficult to be excited into violent motion by the colliding gas atom. A real lattice would therefore be likely to have an effective value of K such that $K \ll 1$.

Without a detailed evaluation, it is difficult to estimate the effect of the attractive part of the surface interaction but it is felt that, since the particle would spend

more time under the influence of the surface, the accommodation coefficient would be appropriately higher in all cases. The effect of the attractive part of the surface interaction has not been evaluated for this model because of the computational effort involved and also because the model is not as realistic as the true three-dimensional models currently under investigation.

PART II. THE DIATOMIC COLLISION

The purpose of this phase of the work was to investigate the effect on the behavior of the gas particle-solid surface system of the conversion of collisional energy to what might be termed internal energy of the incident particle. The internal energy may take on several different forms. A monatomic molecule can be excited to a higher electronic state or even ionized. A diatomic molecule can go into a rotational state, a vibrational state, or a higher electronic state. It may also be dissociated or ionized. In general it will assume some combination of any or all of these possibilities.

As we will use classical mechanics to treat a purely one-dimensional model, the simplest possibility to consider will be that of a diatomic molecule composed of two identical particles which can be excited in a vibrational mode. While we are forced to ignore the more easily excited states such as rotational motion, the qualitative features should be similar. The essential point is that the incident particle can possess energy in some form other than translational energy associated with the center of mass of the particle.

Section II. A. Solution of the Equations of Motion

The model for the solid consists of a semi-infinite chain of particles of mass M interacting harmonically with their individual nearest neighbors through an elastic parameter $K = \dfrac{M\omega_m^2}{4}$ where ω_m is the maximum frequency the lattice will propagate.

If we let a be the equilibrium separation of each pair of particles and $\phi_i(t)$ be the longitudinal displacement of the i^{TH} particle from equilibrium, $i = 0, 1, 2, \cdots$, then the equations of motion become:

$$M\ddot{\phi}_{n+1} = K(\phi_{n+2} + \phi_n - 2\phi_{n+1}), \quad n = 0, 1, 2, \cdots$$

$$M\ddot{\phi}_0 = K(\phi_1 - \phi_0). \tag{II. A. 1}$$

The influence functions for this system of differential-difference equations can be readily found using the methods of PART III, however, recognizing that this model is a special case of the model of PART I, we see that they are given by (I.A. 2) for $\bar{\omega} = K = 0$:

$$\psi_n = 2 \int_0^{\tau} \frac{n\, J_n(\sigma)}{\sigma}\, d\sigma\ , \qquad \tau = \omega_m t\ ,$$

which results in

$$\psi_n = 2 \sum_{\nu = 0}^{\infty} \left(J_{n+2\nu} + J_{n+2\nu+2}\right)\ . \qquad\qquad \text{(II.A. A)}$$

Now consider an incident diatomic gas molecule with masses M_1 and M_2 and bond elastic constant K_1 interacting harmonically with the end ($n = 0$) particle of the lattice with an interaction elastic parameter K_2. Let the equilibrium separation of M_1 and M_2 be a', the equilibrium separation of M_2 and M be a_o, and assume that the interaction between M_2 and M ceases whenever their relative displacement exceeds $a a_o$, where a is the range of interaction parameter. This system is illustrated in Figure 9. If we let $\xi_1(t)$ and $\xi_2(t)$ be the displacements from equilibrium of the masses M_1 and M_2, respectively, and define the following:

mass ratios – – – – – – – – – – – – – $\mu_1 = M_1/M,\ \mu_2 = M_2/M$

elastic parameter ratios – – – – – – – $\beta_1 = K_1/K,\quad \beta_2 = K_2/K$

relative displacement – – – – – – – – $u = \phi_o - \xi_2$

then the equations of motion which are given by

$$M_1 \ddot{\xi}_1 = K_1(\xi_2 - \xi_1)$$

$$M_2 \ddot{\xi}_2 = K_2(\phi_o - \xi_2) + K_1(\xi_1 - \xi_2)$$

$$M \ddot{\phi}_o = K_2(\xi_2 - \phi_o) + K(\phi_1 - \phi_o)$$

$$M \ddot{\phi}_{n+1} = K(\phi_{n+2} + \phi_n - 2\phi_{n+1}),\quad n = 0, 1, 2, \cdots \qquad \text{(II.A. 3)}$$

become

$$4\mu_1 \ddot{\xi}_1 = \beta_1(\xi_2 - \xi_1)$$

$$4\mu_2 \ddot{\xi}_2 = \beta_2(\phi_0 - \xi_2) + \beta_1(\xi_1 - \xi_2)$$

$$4\ddot{\phi}_0 = \beta_2(\xi_2 - \phi_0) + (\phi_1 - \phi_0)$$

$$4\ddot{\phi}_{n+1} = (\phi_{n+2} + \phi_n - 2\phi_{n+1}), \quad n = 0, 1, 2, \cdots$$
(II.A. 4)

where we have used

$$\ddot{f} = \frac{d^2 f}{dt^2} \ , \quad \ddot{f} = \frac{d^2 f}{d\tau^2} \ , \quad \ddot{f} = \omega_m^2 \ddot{f} \ .$$

Assuming that the crystal is initially cold, the initial conditions are:

$$\phi_n(0) = \phi'_n(0) = 0 \ , \quad n = 0, 1, 2, \cdots$$

$$\xi_1(0) \neq 0, \quad \xi_2(0) = -\alpha a_0, \quad \xi'_1(0) \neq 0, \quad \xi'_2(0) \neq 0$$

(II.A. 5)

As previously mentioned, we restrict ourselves to the case $\mu_1 = \mu_2 = \mu$. Taking the Laplace transform of the equations (II.A. 4) we obtain

$$4\mu \left[s^2 \bar{\xi}_1 - s\xi_1(0) - \xi'_1(0) \right] = \beta_1 \left[\bar{\xi}_2 - \bar{\xi}_1 \right]$$

$$4\mu \left[s^2 \bar{\xi}_2 - s\xi_2(0) - \xi_2(0) \right] = \beta_2 \left[\bar{\phi}_0 - \bar{\xi}_2 \right] + \beta_1 \left[\bar{\xi}_1 - \bar{\xi}_2 \right]$$

$$4 s^2 \bar{\phi}_0 = \beta_2 \left[\bar{\xi}_2 - \bar{\phi}_0 \right] + \left[\bar{\phi}_1 - \bar{\phi}_0 \right]$$

$$4 s^2 \bar{\phi}_{n+1} = \bar{\phi}_{n+2} + \bar{\phi}_n - 2\bar{\phi}_{n+1} \ , \quad n = 0, 1, 2, \cdots$$
(II.A. 6)

The last equation is a second order difference equation, i.e.,

$$\bar{\phi}_{n+2} - 2(1 + 2s^2)\bar{\phi}_{n+1} + \bar{\phi}_n = 0, \quad n = 0, 1, 2, \cdots$$

and to solve this we take the laurent-cauchy transform:

$$g(z) = \sum_{n=0}^{\infty} \bar{\phi}_n z^{-n}$$

and obtain

$$g(z) = \frac{z\bar{\phi}_1 + \left[z^2 - 2(1 + 2s^2)z\right]\bar{\phi}_o}{z^2 - 2(1 + 2s^2)z + 1} \tag{II.A. 7}$$

If we set $\text{COSH } \theta = 1 + 2s^2$, $\text{SINH } \theta = 2s\sqrt{1 + s^2}$ we can write

$$g(z) = \frac{z\left[\bar{\phi}_1 - \bar{\phi}_o \text{COSH } \theta\right] + \left[z^2 - z\text{COSH } \theta\right]\bar{\phi}_o}{z^2 - 2z\text{ COSH } \theta + 1}$$

and on inversion we obtain

$$\bar{\phi}_n = \left[\frac{1 - \bar{\phi}_o \text{COSH } \theta}{2 \text{ SINH } \theta} + \frac{\bar{\phi}_o}{2}\right] e^{n\theta} - \left[\frac{\bar{\phi}_1 - \bar{\phi}_o \text{COSH } \theta}{2 \text{ SINH } \theta} - \frac{\bar{\phi}_o}{2}\right] e^{-n\theta} \tag{II.A. 8}$$

Boundedness of the solution for large n gives us the condition

$$\bar{\phi}_1 - \bar{\phi}_o\left[\text{COSH } \theta - \text{SINH } \theta\right] = 0$$

or

$$\bar{\phi}_1 = \left[s - \sqrt{1 + s^2}\right]^2 \bar{\phi}_o . \tag{II.A. 9}$$

Hence

$$\bar{\phi}_n = \bar{\phi}_o e^{-n\theta} = \bar{\phi}_o\left[s - \sqrt{1 + s^2}\right]^{2n} . \tag{II.A. 10}$$

We now have four equations, namely (II.A. 9) and the first three equations of (II.A. 6), to solve for the four unknowns $\bar{\xi}_1$, $\bar{\xi}_2$, $\bar{\phi}_o$ and $\bar{\phi}_1$. Solving these, we obtain

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$$u(s) = \overline{\phi}_o(s) - \overline{\xi}_2(s)$$

$$= \frac{-8s\mu \left[\beta_1 + 4\mu s^2\right]\left[s\xi_2(0) + \xi_2'(0)\right] + \beta_1\left[s\xi_1(0) + \xi_1'(0)\right]}{\left[\beta_1 + \beta_2 + 4\mu s^2\right]\left[\beta_2(\sqrt{1+s^2} - s) + 2s\right]\left[\beta_1 + 4\mu s^2\right] - \\ - \beta_2^2\left[\beta_1 + 4\mu s^2\right]\left[\sqrt{1+s^2} - s\right] + \beta_1^2\left[\beta_2(\sqrt{1+s^2} - s) + 2s\right]}$$

(II.A. 11)

Now if

$$\overline{u}(s) = \sum_{n=0}^{\infty} c_n \frac{2}{s}\left[\sqrt{1+s^2} - s\right]^n$$

(II.A. 12)

then

$$u(\tau) = \sum_{n=0}^{\infty} c_n \psi_n(\tau)$$

(II.A. 13)

where the ψ_n are given by equation (II.A. 2). If we let $x = \left[\sqrt{1+s^2} - s\right]$ we can easily show that

$$s = \frac{1 - x^2}{2x}$$

$$\sqrt{1 + s^2} = \frac{1 + x^2}{2x}$$

Then we can write equation (II.A. 12) in the form

$$\frac{2}{s}\overline{u}(s) = f(x) = \sum_{n=0}^{\infty} c_n x^n$$

and we have the straightforward task of determining the coefficients in a power series expansion of $f(x)$ about the point $x = 0$. If we define $\rho = \frac{\beta_1}{\mu}$, the coefficients c_n are functions of ρ, β_2, and μ, and can be determined either analytically or numerically

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for given values of these parameters. The latter technique was used in this case and the problem was programmed for the IBM 7090 computer of the Marshall Space Flight Center.

Because of the inability of the simple one dimensional chain to represent a real crystal, it was felt that a thorough analysis of the data would be unfruitful. Two aspects were considered to be of interest; they were the trapping curves and the accommodation coefficients. Lack of time due to programming difficulties restricted the analysis to only one phase. As the accommodation was of more immediate interest this aspect of the behavior of the system was chosen for investigation.

Section II.B. Accommodation Coefficients

As in Section I.C. the accommodation coefficient is defined by the equation

$$a.c. = \frac{K_i - K_f}{K_i} \tag{I.C. 1}$$

In any experimental measurement based on molecular beam techniques and using mechanical velocity selectors, the internal energy of the gas particles will not plan an important role so we take the kinetic energies appearing in equation (I.C. 1) to be the translational kinetic energies of the gas molecule. Thus the accommodation coefficient will be given by

$$a.c. = 1 - \left[\frac{\dot{\xi}_1(\tau_c) + \dot{\xi}_2(\tau_c)}{\dot{\xi}_1(0) + \dot{\xi}_2(0)} \right]^2 \tag{II.B. 1}$$

where τ_c is the reduced time corresponding to the end of the collision.

The translational velocity of the gas molecule as a function of time can be found by integrating the sum of the first two of equations (II.A. 3)

$$\ddot{\xi}_1(t) + \ddot{\xi}_2(t) = \frac{K_2}{M_1} (\phi_o - \xi_2) = \frac{K_2}{M_1} u(t) \tag{II.B. 2}$$

with respect to time. We have

$$\frac{d^2 \xi_1}{d\tau^2} + \frac{d^2 \xi_2}{d\tau^2} = \frac{1}{\omega_m^2} \left[\frac{d^2 \xi_1}{dt^2} + \frac{d^2 \xi_2}{dt^2} \right] = \frac{K_2}{\omega_m^2 M_1} \, u(\tau)$$

$$\frac{d\xi_1}{d\tau} + \frac{d\xi_2}{d\tau} = \xi_1'(\tau) + \xi_2'(\tau) = \xi_1'(0) + \xi_2'(0) + \frac{\beta_2}{4\mu} \int_0^\tau u'(s)\,ds$$

Again we can write

$$u(\tau) = u(0)\,\frac{df}{d\tau} + u'(0)\,f(\tau)$$

so we have

$$\frac{\xi_1'(\tau) + \xi_2'(\tau)}{\xi_1'(0) + \xi_2'(0)} = 1 + \frac{\beta_2}{4\mu\left[\xi_1'(0) + \xi_2'(0)\right]} \int_0^\tau \left[u(0)\,\frac{df}{ds} + u(0)\,f'(s) \right] ds$$

$$(\text{II.B. } 3)$$

Now by choosing $\alpha = 0$ and $\xi_1(\theta) = 0$ we limit our discussion to the case of a purely repulsive interaction with an initially uncompressed molecule. This represents the high initial velocity case in which the attractive part of the binding potential plays a negligible role. Because of the cold surface assumption

$$u'(\theta) = \phi_0'(\theta) - \xi_2'(0) = -\xi_2'(0)$$

and so we obtain

$$\frac{\dot{\xi}_1 + \dot{\xi}_2}{\xi_1(\theta) + \xi_2(\theta)} = \frac{\xi_1' + \xi_2'}{\xi_1'(0) + \xi_2'(0)} = 1 - \frac{\beta_2 \, \xi_2'(0)}{4\mu\left[\xi_1'(\theta) + \xi_2'(\theta)\right]} \int_0^\tau f(s)\,ds$$

$$(\text{II.B. } 4)$$

We can further simplify our task without loss of generality by assuming $\xi_1'(\theta) = 0$. In this case we have the accommodation coefficient given by

$$a.c. = 1 - \left[1 - \frac{\beta_2}{4\mu} \int_0^{\tau_c} f(s) \, ds \right]^2 \qquad \text{(II.B. 5)}$$

where τ_c is the reduced time corresponding to the first zero of the integral for nonzero time.

Referring to Figures 10. and 11. for $\mu = \frac{1}{2}$ and $\mu = \frac{1}{4}$, respectively, we see that the effect of exciting the molecule into vibrational motion is to increase the accommodation coefficient for small values of β_2 over that of the monatomic collision and to decrease the accommodation coefficient for larger values of β_2. The effect is more pronounced for lighter molecules and for molecules with weaker molecular bonds. Due to the tendency of the simple one dimensional chain to collapse, i.e., to have a permanent displacement of the chain, the curves were not extended to smaller values of β_2 since these values correspond to cases for which $u(\tau)$ exceeds $a a_0$ but for which the velocity of the molecule is positive , i.e., in the direction of the end of the chain. In such a case the molecule could collide again with the chain and this would not represent a physically realistic system.

Inasmuch as the curves are compared with those for a monatomic molecule under identical circumstances, it is felt that the effect of the excitation of the incident particle into internal motion is adequately represented. However it is not felt that it would be worthwhile to pursue this particular model much further due to its extreme complexity and because it only indicates qualitative trends. If the diatomic collision is of further interest a better model for the solid, such as that in PART I, should be used.

PART III. THE MATHEMATICAL TECHNIQUES

This section of the report is concerned with the analysis of the differential-difference equations which occur in the description of physical systems of the type which appeared in PARTS I. and II. The most versatile formulation of such a system is in terms of its response to impulsive inputs. The response to an arbitrary forcing function can be synthesized by a Faltung integral, and any free wave solutions can be obtained easily from asymptotic expansions of the impulsive responses. Transform techniques are used throughout, and these techniques permit infinite, semi-infinite, and finite bounds on the lattice variables to be treated with equal facility. Applications are indicated with each system, but physical evaluation is reserved for treatment elsewhere.

The basic transform used is the Laplace-Stieltjes transform.

$$f(s) = \int_0^\infty e^{-sx} \, dg(x) \, , \qquad g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{e^{sx}}{s} \, f(s) \, ds \qquad \text{(III. 1)}$$

Where the Stieltjes integration is over the variable x. If

$$dg(x) = \phi(x) \, dx$$

then the transform reduces to the ordinary Laplace transform, i.e.,

$$f(s) = \int_0^\infty e^{-sx} \phi(x) \, dx \, , \qquad \phi(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{sx} f(s) \, ds \qquad \text{(III. 2)}$$

If

$$dg(x) = e^{s\epsilon} \phi(x - \epsilon) \, d\left[x + m - \epsilon\right]$$

where $0 < \epsilon < 1$, $[x]$ is the greatest integer in x, and m is an arbitrary integer, then the transform reduces to the Laurent-Cauchy transform, i.e., $\rho = e^{-s}$

$$f(\rho) = \sum_{m=0}^{\infty} \phi(m) \, \rho^m \quad , \quad \phi(K) = \frac{1}{2\pi i} \oint_c \rho^{-K-1} f(\rho) \, d\rho \qquad \text{(III. 3)}$$

Where C enclosed the singularities of $f(\rho)$. Properties of the above transform are easily derivable from the definition. The derivation of several transform pairs is given in the appendix.

Section III.A. The Sodium Chloride Lattice

As a relatively simple example which will demonstrate the techniques used in problems with only one lattice variable, consider the one dimensional, infinite sodium chloride type crystal with harmonic nearest neighbor interactions, excited by a longitudinal or transverse impulse at the center of the crystal.

Let $u_m(t)$, $V_m(t)$, $-\infty < m < \infty$ denote the displacements of the particles of masses m_o, m_1, from equilibrium. Let u_o be the displacement of the particle at the center of the crystal, and $k = m_o \omega^2$ be the harmonic interaction between the nearest neighbors. Since the crystal is excited from the center, we have the symmetry relations $V_{-m-1} = V_m$, $u_{-m} = u_m$, $m = 0, 1, \cdots$. The equations of motion are then

$$m_o \ddot{u}_o = k \left[2V_o - 2u_o \right]$$

$$m_o \ddot{u}_{n+1} = k \left[V_{n+1} + V_n - 2 u_{n+1} \right]$$

$$m_1 \ddot{V}_n = k \left[u_{n+1} + u_n - 2 V_n \right]$$

$$V_n(0) = \dot{V}_n(0) = u_{n+1}(0) = \dot{u}_{n+1}(0) = 0$$

$$n = 0, 1, 2, \cdots \qquad u_o(0) = 0 \quad \dot{u}_o(0) = 1 \qquad \text{(III.A. 1)}$$

where $\dot{g} = \dfrac{dg}{dt}$

If we let $\tau = 2\omega t$ be the reduced time, $\mu = \dfrac{m_o}{m_1}$ be the mass ratio, $\bar{u}_n(s)$, $\bar{V}_n(s)$ be the (tau) Laplace transforms of $u_n(\tau)$, $V_n(\tau)$, we have, on applying this transform to

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the above equations

$$(2s^2 + 1)\,\bar{u}_o = \bar{V}_o + 2I_o \qquad\qquad I_o = \frac{1}{2\omega}$$

$$2(2s^2 + 1)\,\bar{u}_{n+1} = \bar{V}_{n+1} + \bar{V}_n$$

$$2(2s^2 + \mu)\,\bar{V}_n = \mu\left[\bar{u}_{n+1} + \bar{u}_n\right]$$

$$n = 0, 1, 2, \cdots \qquad\qquad\qquad\qquad\qquad\qquad \text{(III.A. 2)}$$

Now let $F_o(\rho, s), F_1(\rho, s)$ be the Laurent-Cauchy transforms of $\bar{u}_n(s)$, $\bar{V}_n(s)$. Applying this transform to the above equations, and using the shift theorem derived in the appendix, we have, in matrix notation

$$\begin{pmatrix} \mu(\rho + 1) & -2(2s^2 + \mu) \\ -2\rho(2s^2 + 1) & (\rho + 1) \end{pmatrix} \begin{pmatrix} F_o \\ F_1 \end{pmatrix} = \begin{pmatrix} \rho\mu\,\bar{u}_o \\ -\rho\left[(2s^2 + 1)u_o + 2I_o\right] \end{pmatrix}$$

Solving this system by Cramer's rule, and using the definition $\text{COSH}\,a_o = \dfrac{2(2s^2 + 1)(2s^2 + \mu)}{\mu} - 1$,

we have

$$F_o = \bar{u}_o\left\{\frac{\rho(\rho - \text{COSH}\,a_o)}{\Delta}\right\} - \frac{4I_o(2s^2 + \ )}{\text{SINH}\,a_o}\left\{\frac{\rho\,\text{SINH}\,a_o}{\Delta}\right\}$$

$$F_1 = \left[(2s^2 + 1)\,\bar{u}_o - 2I_o\right]\left\{\frac{\rho(\rho - \text{COSH}\,a_o)}{\Delta}\right\} - \left[\frac{(1 - \text{COSH}\,a_o)(2s^2 + 1)u_o + (1 + \text{COSH}\,a_o)\,2I_o}{\text{SINH}\,a_o}\right]$$

$$\left\{\frac{\rho\,\text{SINH}\,a_o}{\Delta}\right\} \qquad\qquad\qquad \text{(III.A. 3)}$$

$$\Delta = \rho^2 - 2\rho\,\text{COSH}\,a_o + 1$$

These equations can now be inverted by use of the transform pairs given in the appendix. Doing this inversion, we have

$$\bar{u}_n = \bar{u}_o \, \text{COSH} \, na_o \; - \; \frac{4I_o(2s^2 + \mu)}{\mu \, \text{SINH} \, a_o} \; \text{SINH} \, na_o$$

$$\bar{V}_n = \left[(2s^2 + 1)\bar{u}_o - 2I_o\right] \text{COSH} \, na_o \; - \; \left[\frac{(1 - \text{COSH} \, a_o)(2s^2 + 1)\bar{u}_o + (1 + \text{COSH} a_o)2I_o}{\text{SINH} \, a_o}\right] \text{SINH} \, na_o$$

$$(\text{III.A. } 4)$$

In order to determine $\bar{u}_o$, we need another condition. If the crystal had been of finite length, we could use the conditions on $\bar{V}_n$, $\bar{u}_n$ at the end of the crystal to determine $\bar{u}_o$. In our case we require that as $n \to \infty$, $\bar{u}_n$ and $\bar{V}_n$ be bounded in absolute value. Since $\text{Re}(s) > 0$ the only way that this is possible is for the coefficients of the positive exponents of the cosh a_o and sinh a_o terms in the above transforms to be zero. Using this conditions, we have finally for the Laplace transforms

$$\bar{u}_n = \frac{4I_o(2s^2 + \mu)}{\mu \, \text{SINH} \, a_o} \; (\Gamma)^n$$

$$(\text{III.A. } 4)$$

$$\bar{V}_n = \frac{2I_o}{\text{SINH} \, a_o} \; (\Gamma)^n (1 + \Gamma)$$

$$\Gamma = \text{COSH} \, a_o - \text{SINH} \, a_o = e^{-a_o}$$

Using the relation

$$\frac{1}{\text{SINH} \, a_o} \left[\text{COSH} \, a_o - \text{SINH} \, a_o\right]^n = \frac{1}{\pi} \int_0^\pi \frac{\text{COS} \, n\theta \, d\theta}{\text{COSH} \, a_o - \text{COS} \, \theta}$$

We can write the above transforms in the following form:

$$\bar{u}_n = \frac{4I_o(2s^2 + \mu)}{\mu \pi} \int_0^\pi \frac{\text{COS} \, n\theta \, d\theta}{\text{COSH} \, a_o - \text{COS} \, \theta}$$

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$$V_n = \frac{2I_o}{\pi} \int_0^\pi \frac{[COS\, n\theta + COS\,(n+1)\theta]\; d\theta}{COS\, a_o - COS\, \theta} \qquad\qquad (III.A.\ 5)$$

Now

$$COSH\, a_o - COS\, \theta = \frac{2(2s^2 + 1)(2s^2 + \mu)}{\mu} - 1 - COS\, \theta$$

$$= \frac{8}{\mu}\,(s^2 + \omega_1^2)(s^2 + \omega_2^2)$$

where

$$\omega_{1,2} = \frac{1}{2}\left\{ (1 + \mu) \pm \sqrt{(\mu^2 + 2\mu\, COS\, \theta + 1)}\right\}^{1/2}$$

also

$$\frac{as^2 + b}{(s^2 + \omega_1^2)(s^2 + \omega_2^2)} = \frac{a\omega_2^2 - b}{\omega_2(\omega_2^2 - \omega_1^2)}\left\{\frac{\omega_2}{s^2 + \omega_2^2}\right\} - \frac{a\omega_1^2 - b}{\omega_1(\omega_2^2 - \omega_1^2)}\left\{\frac{\omega_1}{s^2 + \omega_1^2}\right\}$$

Using these relations in the above transforms, and then taking the inverse Laplace trans-
form of the terms $\dfrac{\omega}{s^2 + \omega^2}$ we have the following solutions

$$u_n(\tau) = \frac{I_o}{\pi} \int_0^\pi \frac{COS\, n\theta}{\omega_2^2 - \omega_1^2}\left\{\frac{\omega_2^2 - \mu/2}{\omega_2}\,SIN\,\omega_2\tau - \frac{\omega_1^2 - \mu/2}{\omega_1}\,SIN\,\omega_1\tau\right\} d\theta$$

$$V_n(\tau) = \frac{\mu I_o}{4\pi} \int_0^\pi \frac{COS\, n\theta + COS(n+1)\theta}{\omega_2^2 - \omega_1^2}\left\{\frac{1}{\omega_1}\,SIN\,\omega_1\tau - \frac{1}{\omega_2}\,SIN\,\omega_2\tau\right\} d\theta$$

$$\qquad\qquad (III.A.\ 6)$$

Section III.B. The Polyatomic Lattice

As a more general example consider the one dimensional, semi-infinite polyatomic
crystal with nearest neighbor interactions, excited by a longitudinal or transverse impulse

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at the end of the crystal. Let us have a group of r different atoms and n different harmonic interactions which repeats itself to infinity. Let us introduce two terms, which from a physical point of view represent three dimensional effects in this one dimensional problem. First, let each type of atom move in a fixed harmonic potential. This fixed potential simulates the restorative effect of the crystal bulk, and prevents the collapse of the model. Second, let each type of atom move under the influence of a linear, velocity dependent force. This dissipative term simulates the flow of energy into the bulk of the crystal.

Let $u_n^l(t)$, $0 \leq l \leq n$, $0 \leq n < \infty$ denote the displacement from equilibrium of the particle of mass m_l $0 \leq l \leq r$ in the n^{TH} group. Clearly l is the index within the polyatomic group, and n is the index of the different groups. Let $k_l = m_l \, \omega_l^2$ be the harmonic interaction between the l and the $l + 1^{ST}$ particles $0 \leq l < r$ with the understanding that the $r + 1^{ST}$ particle is the o^{TH} particle of the next group. Let $\bar{k}_l$ and K_l be the fixed harmonic interaction and velocity dependent parameters, respectively for the l^{TH} particle. The equations of motion are then

$$m_o \ddot{u}_o^o = k_o(u_o^1 - u_o^o) - \bar{k}_o u_o^o - K_o \dot{u}_o^o$$

$$m_o \ddot{u}_{n+1}^o = k_o(u_{n+1}^1 - u_{n+1}^o) + k_r(u_n^r - u_{n+1}^o) - \bar{k}_o u_{n+1}^o - K_o \dot{u}_{n+1}^o$$

$$0 \leq n < \infty$$

$$\text{(III.B. 1)}$$

$$m_r \ddot{u}_n^r = k_r(u_{n+1}^o - u_n^r) + k_{r-1}(u_n^{r-1} - u_n^r) - \bar{k}_r u_n^r - K_r \dot{u}_n^r$$

$$0 \leq n < \infty$$

$$m_Q \ddot{u}_n^Q = k_Q(u_n^{Q+1} - u_n^Q) + k_{Q-1}(u_n^{Q-1} - u_n^Q) - \bar{k}_Q u_n^Q - K_Q \dot{u}_n^Q$$

$$1 \leq Q \leq r - 1, \quad 0 \leq n < \infty$$

$$\dot{f} = \frac{df}{dt} \; , \quad u_n(0) = \dot{u}_n(0) = 0 \quad \begin{cases} 1 \leq n < \infty \, , \, 0 \leq l \leq r \\ n = 0 \quad 1 \leq l \leq r \end{cases} \qquad \begin{aligned} \overset{o}{u}_o(0) &= 0 \\ \overset{o}{u}_o(0) &= 1 \end{aligned}$$

Let $F_i(\rho, s)$, $0 \leq i \leq r$ be the double Laurent-Cauchy, Laplace transform of $u_n^i(t)$, $0 \leq i \leq r$, $0 \leq n < \infty$. Taking this transform of the above equations we have, in matrix notation

$$\underline{\underline{A}} \; \underline{F} = \underline{I}$$

$$\underline{\underline{A}} = \begin{pmatrix} l_o \rho & -k_o \rho & 0 & . & . & . & 0 & -k_r \\ -k_o & l_1 & -k_1 & . & & & & 0 \\ 0 & -k_1 & . & . & . & & & . \\ . & & . & . & . & . & & . \\ . & & & . & . & . & . & . \\ . & & & & . & . & . & 0 \\ 0 & & & & & . & l_{r-1} & -k_{r-1} \\ -\rho k_r & 0 & . & . & . & 0 & -k_{r-1} & l_r \end{pmatrix}$$

$$\underline{F} = \begin{pmatrix} F_1(\rho, s) \\ . \\ . \\ . \\ . \\ . \\ F_r(\rho, s) \end{pmatrix} , \quad \underline{I} = \begin{pmatrix} \rho k_r \overset{o}{u}_o + \rho \\ 0 \\ . \\ . \\ . \\ 0 \\ -\rho k_r \overset{o}{u}_o \end{pmatrix}$$

$$l_l = m_l s^2 + K_l s + k_l + k_{l-1} + \overline{k}_l$$
$$0 \leq l \leq r$$
$$k_{-1} = k_r$$

This system of equations may be solved by Cramer's rule. By elementary determinant manipulation, we may remove the ρ dependence from the determinant of the coefficients, and write it as

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$$\text{DET}\ (\underline{\underline{A}})\ =\ (-)^r k_r \left| \begin{array}{cccccc} -k_o & 0 & . & . & . & 0 \\ & & & & & . \\ & \multicolumn{4}{c}{X} & . \\ & & & & & 0 \end{array} \right| (\ \rho^2 - 2\rho\ \text{COSH}\ a_o + 1)$$

$$\text{COSH}\ a_o\ =\ \cfrac{Y\ -\ k_r^2\ X}{2(-)^{r+1} k_r \left| \begin{array}{cccccc} -k_o & 0 & . & . & . & 0 \\ & & & & & . \\ & \multicolumn{4}{c}{X} & . \\ & & & & & 0 \end{array} \right|}$$

$$X\ =\ \left| \begin{array}{ccccccccc} i_1 & -k_1 & 0 & . & . & . & . & & 0 \\ -k_1 & l_2 & -k_2 & & & & & & . \\ . & . & . & . & . & & & & . \\ . & & . & . & . & . & & & . \\ . & & & . & . & . & . & & 0 \\ . & & & & . & . & . & & -k_{r-3} \\ . & & & & & . & -k_{r-1} & & l_{r-1} \\ 0 & . & . & . & . & . & 0 & & -k_{r-1} \end{array} \right|$$

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$$Y = \begin{vmatrix} I_o & -k_o & 0 & . & . & . & 0 \\ -k_1 & I_1 & . & & & & . \\ . & . & . & . & & & . \\ . & & . & . & . & & . \\ . & & & . & . & . & . \\ . & & & & . & . & 0 \\ . & & & & . & . & -k_{r-1} \\ 0 & . & . & . & 0 & -k_{r-1} & I_r \end{vmatrix}$$

Now each numerator expression in Cramer's rule will be of the form

$$A_i \rho^2 + B_i \rho \quad , \quad 0 \le i \le r$$

thus making each inversion of the form

$$F_i(\rho, s) = \frac{A_i \rho^2 + B_i \rho}{DET(\underline{A})} \quad , \quad 0 \le i \le r$$

By rearranging terms, we may write the above inversion as

$$F_i(\rho, s) = C_i \frac{\rho(\rho - COSH\, a_o)}{\rho^2 - 2\rho\, COSH\, a_o + 1} + D_i \frac{\rho\, SINH\, a_o}{\rho^2 + 2\rho\, COSH\, a_o + 1}$$

$$(III.B.\ 2)$$

where C_i, D_i are in general functions of $u_o^o(s)$. Inverting this expression we have for the Laplace transforms

$$\bar{u}_n^i (s) = C_i \; \text{COSH} \; na_o + D_i \; \text{SINH} \; na_o$$

$$0 \le i \le r \; , \quad 0 \le n < \infty \qquad\qquad \text{(III.B. 3)}$$

As in the introductory example, we require that as $n \to \infty$, $\bar{u}_n^i (s)$ be bounded in absolute value. From this requirement we have

$$C_i (u_o^o) = - D_i (u_o^o) \; , \quad 0 \le i \le r \qquad\qquad \text{(III.B. 4)}$$

which yields an expression for u_o^o . The final Laplace transforms are

$$\bar{u}_n^i (s) = C_i (u_o^o) \; (\text{COSH} \; na_o - \text{SINH} \; na_o)$$

$$= C_i (u_o^o) \; (\text{COSH} \; a_o - \text{SINH} \; a_o)^n \quad 0 \le i \le r \, , 0 \le n < \infty$$

$$\text{(III.B. 5)}$$

We have as yet been unable to perform the Laplace inversion in general, consequently, in any particular problem the tractability of this task depends on an intelligent, and perhaps fortunate, arrangement of terms. This problem will receive further attention.

Section III.C. Higher Dimensional Models

The method of solving the higher dimensional models is an extension of a method developed by Bateman and presented by Pinney. We will consider differential–difference equations of the form.

$$F \left[W \left(\frac{d}{dt} \right) \phi \; , \; u_1 (\Delta P_1) \phi \, , \, u_2 (\Delta P_2) \phi \, , \, \cdots \, , \, u_n (\Delta P_n) \phi \right] = 0$$

$$\Delta_{P_i} \phi_{P_i} = \phi_{P_i + 1} - \phi_{P_i - 1} \qquad\qquad \text{(III.C. 1)}$$

where $u_i(x)$ are polynomials in their arguments, and ϕ , the solution, is a function of P_i , t. Now consider the partial differential equation.

$$F \left[W (\frac{d}{dt}) \psi \ , \ V_1 (\frac{\partial}{\partial x_1}) \psi \ , \ V_2 (\frac{\partial}{\partial x_2}) \psi \ , \ \cdots \ , \ V_n (\frac{\partial}{\partial x_n}) \psi \right] = 0$$

(III.C. 2)

The solution $\psi = \psi (x_i, t)$ will, in general, possess some arbitrary properties. Now if we let these arbitrary properties depend on the indices P, Q, r in such a way that

$$V_i (\frac{\partial}{\partial x_i}) \psi (s_i, t, P_i) = U_i (\Delta P_i) \psi (s_i, t, P_i) \ , \quad \text{ALL } i \quad \text{(III.C. 3)}$$

then it is clear that ψ as a function of P_i, t is a solution of the differential–difference equation. The x_i become arbitrary parameters, and we let them take on any particular values which will simplify the solutions.

As a simple example which will demonstrate the above technique, consider the three dimensional, semi-infinite, homogeneous cubic lattice, with harmonic nearest neighbor interactions, excited by a normal impulse at the center of the surface.

Let $u_{P,Q,r}(t)$, $- \infty < p, Q < \infty$, $0 \le r < \infty$ denote the displacement, in a direction normal to the surface, of the particle located at the P, Q, r lattice point. Let m be the mass of the particle, $k_1 = m \omega_1^2$ be the harmonic transverse interaction, and $k_2 = m \omega_2^2$ be the harmonic longitudinal interaction. Since the crystal is excited from the center, we have the symmetry relations $u_{P,Q,r} = u_{P,-Q,r} = u_{-p,q,r} = u_{-p,-Q,r}$. The equations of motion are then

$$m \frac{d^2 u_{P,Q,r}(t)}{dt^2} = k_1 [\Delta_P^2 + \Delta_Q^2] u_{P,Q,r} + k_2 \Delta_r^2 u_{P,Q,r} \quad \begin{array}{l} -\infty < P,Q < \infty \\ 1 \le r < \infty \end{array}$$

$$m \frac{d^2 u_{P,Q,r}(t)}{dt^2} = k_1 [\Delta_P^2 + \Delta_Q^2] u_{P,Q,r} + k_2 [u_{P,Q,1} - u_{P,Q,0}]$$

$$- \infty < P,Q < \infty, \quad r = 0$$

(III.C. 4)

$$\Delta_i^2 u_i = u_{i+1} + u_{i+1} - 2u_i$$

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Now let $u_{P,Q,r}(t)$ be a function of the fictitious variables x_i , and require that

$$\frac{\partial^2}{\partial x_1^2} u_{P,Q,r} = \omega_1^2 \Delta_P^2 u_{P,Q,r} \qquad -\infty < P < \infty$$

$$\frac{\partial^2}{\partial x_2^2} u_{P,Q,r} = \omega_1^2 \Delta_Q^2 u_{P,Q,r} \qquad -\infty < Q < \infty$$

$$\frac{\partial^2}{\partial x_3^2} u_{P,Q,r} = \omega_2^2 \begin{cases} \Delta_r^2 u_{P,Q,r} & 1 \le r < \infty \\[2mm] u_{P,Q,1} - u_{P,Q,0} & r = 0 \end{cases}$$

$$\text{(III.C. 5)}$$

Using this transformation from P,Q,r to x_1, x_2, x_3, the equations of motion become

$$\frac{\partial^2 u_{P,Q,r}}{\partial t^2} = \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right] u_{P,Q,r}$$

$$\text{(III.C. 6)}$$

This is the scalar wave equation which, on applying Huyghen's Principle, is seen to have the following general solution:

$$u_{P,Q,r}(x_1, x_2, x_3, t) = \frac{d}{dt}(I_1) + I_2$$

$$I_{1,2} = \frac{t}{4\pi} \int_\Omega f_{P,Q,r}^{(1),(2)} (l, m, n)\, d\Omega \qquad \text{(III.C. 7)}$$

where

$$l = x_1 + t\, COS\theta,\ m = x_2 + t\, SIN\theta\, COS\phi\ ,\ n = x_3 + t\, SIN\theta\, SIN\phi$$

$f_{P,Q,r}^{(1)}$, $f_{P,Q,r}^{(2)}$ are the arbitrary functions which are assigned the indices P,Q,r.
They satisfy the relations

$$f^{(1)}_{P,Q,r}(x_1,x_2,x_3) = u_{P,Q,r}(x_1,x_2,x_3,0)$$

$$f^{(2)}_{P,Q,r}(x_1,x_2,x_3) = \frac{\partial}{\partial t} u_{P,Q,r}(x_1,x_2,x_3,t)\Big|_{t=0}$$

(III.C. 8)

the initial conditions of $u_{P,A,r}(t)\Big|_{t=0}$ are

$$u_{P,Q,r}(0) = 0$$

$$\frac{d}{dt} u_{P,Q,r}(t)\Big|_{t=0} = \delta_{P,0}\, \delta_{Q,0}\, \delta_{r,0} \quad \text{(III.C. 9)}$$

For fixed values of the x_i, $f^{(1)}_{P,Q,r}$, $f^{(2)}_{P,Q,r}$ will satisfy these same initial conditions. Let these values be $x_1 = x_2 = x_3 = 0$, i.e.

$$f^{(1)}_{P,Q,r}(0,0,0) = 0$$

$$f^{(2)}_{P,Q,r}(0,0,0) = \delta_{P,0}\, \delta_{Q,0}\, \delta_{r,0} \quad\quad \text{(III.C. 10)}$$

Since all other values of the x_i no longer have meaning in the problem, we may set $f^{(1)}_{P,Q,r} = 0$ for all x_i. The transformation equations from P,Q,r to x_1,x_2,x_3 become

$$\frac{\partial^2 f^{(2)}_{P,Q,r}}{\partial x_1^2} = \omega_1^2\, \Delta_P^2\, f^{(2)}_{P,Q,r} \quad\quad -\infty < P < \infty$$

$$\frac{\partial^2 f^{(2)}_{P,Q,r}}{\partial x_2^2} = \omega_1^2\, \Delta_Q^2\, f^{(2)}_{P,Q,r} \quad\quad -\infty < Q < \infty$$

$$\frac{\partial^2 f_{P,Q,r}}{\partial x_3^2} = \omega_2^2 \begin{cases} \Delta_r^2\, f^{(2)}_{P,Q,r} & 1 \le r < \infty \\ f^{(2)}_{P,Q,0} & r = 0 \end{cases} \quad \text{(III.C. 11)}$$

Now let us assume a separation of variables of the form

$$f^{(2)}_{P,Q,r} (x_1, x_2, x_3) = X^{(1)}_P(x_1) \ X^{(2)}_Q(x_2) \ X^{(3)}_r(x_3) \qquad \text{(III.C. 12)}$$

With this separation, the transformation equations reduce to a set of one dimensional differential-difference equations, i.e.

$$\frac{d^2 X^{(1)}_P}{dx_1^2} = \omega_1^2 \Delta_P^2 X^{(1)}_P \qquad X^{(1)}_P(0) = \delta_{P,0} \qquad -\infty < P < \infty$$

$$\frac{d^2 X^{(2)}_Q}{dx_2^2} = \omega_1^2 \Delta_Q^2 X^{(2)}_Q \qquad X^{(2)}_Q(0) = \delta_{Q,0} \qquad -\infty < Q < \infty$$

$$\frac{d^2 X^{(3)}_r}{dx_3^2} = \omega_2^2 \begin{cases} \Delta_r^2 X^{(3)}_r & 1 \leq r < \infty \\ X^{(3)}_1 - X^{(3)}_o & r = 0 \end{cases} \qquad X^{(3)}_r(0) = \delta_{r,0}$$

$$\text{(III.C. 13)}$$

By applying the methods of the section on one dimensional problems, we easily obtain the following solutions for the above set of equations.

$$X^{(1)}_P(x_1) = J_{2P}(2\omega_1 x_1)$$

$$X^{(2)}_Q(x_2) = J_{2Q}(2\omega_1 x_2)$$

$$X^{(3)}_r(x_3) = J_{2r}(2\omega_2 x_3) + J_{2(r+1)}(2\omega_2 x_3)$$

$$\text{(III.C. 14)}$$

Using these solutions for $f^{(2)}_{P,Q,r}(x_1, x_2, x_3)$, putting $f^{(2)}_{P,Q,r}$ in the wave equation integral, and setting $x_1 = x_2 = x_3 = 0$, we have the following solution

$$u_{P,Q,r}(t) = \frac{t}{4\pi} \int_0^{2\pi} \int_0^{\pi} [\, J_{2r}(2\omega_2 t \cos\theta) + J_{2(r+1)}(2\omega_2 t \cos\theta)\,]$$

$$\times\ J_{2P}(2\omega_1 t \sin\theta \cos\phi)\, J_{2Q}(2\omega_1 t \sin\theta \sin\phi)\, \sin\theta\, d\theta\, d\phi\,.$$

$$(\text{III.C. } 15)$$

It is instructive to determine the extent to which the lattice displacements for the model of Kinzer and Chambers approximate those for the simple cubic lattice, equation (III.C. 15). For simplicity we will consider only the displacement of the lattice particle located at the origin. For the three dimensional model

$$\phi_o^{(3)} = \frac{2\omega_2 t}{4\pi} \int_0^{2\pi} \int_0^{\pi} [\, J_o(2\omega_2 t \cos\theta) + J_2(2\omega_2 t \cos\theta)\,]$$

$$\times\ J_o(2\omega_1 t \sin\theta \cos\phi)\, J_o(2\omega_1 t \sin\theta \sin\phi)\, \sin\theta\, d\theta\, d\phi$$

$$(\text{III.C. } 16)$$

while for the one dimensional model

$$\phi_o^{(1)} = e^{-k\tau} \int_0^{\tau} J_o\, [\,(\bar{\omega}^2 - k^2)^{1/2}(\tau^2 - \sigma^2)^{1/2}\,]\, [\,J_o(\sigma) + J_2(\sigma)\,]\, d\sigma$$

$$(\text{III.C. } 17)$$

In this expression let $\sigma = 2\omega_1 t \cos\theta$. Then we have, after some manipulation,

$$\phi_o^{(1)} = \frac{t}{4\pi} \int_0^{\pi} [\, J_o(2\omega_1 t \cos\theta) + J_2(2\omega_1 t \cos\theta)\,]\, \sin\theta\, d\theta$$

$$\times\ \left\{ 4\pi\omega_1 J_o\left(2\omega_1\left(\bar{\omega}^2 - k^2\right)^{1/2} t \sin\theta\right) e^{-2\omega_1 kt} \right\}$$

$$(\text{III.C. } 18)$$

and

$$\phi_0^{(3)} = \frac{t}{4\pi} \int_0^\pi [J_0(2\omega_2 t \cos\theta) + J_2(2\omega_2 t \cos\theta)] \sin\theta \, d\theta$$

$$\times \{ \int_0^{2\pi} 2\omega_2 J_0(2\omega_1 t \sin\theta \cos\phi) J_0(2\omega_1 t \sin\theta \sin\phi) d\phi \} .$$

(III.C. 19)

Now for the three dimensional model let $\Omega_3 = 2\omega_1$ and $\Omega_2 = 2\omega_2$ and for the one dimensional model let $\Omega_1 = 2\omega_1$. We need only compare the terms in braces in expressions (III.C. 18) and (III.C. 19). Denoting these by { 1 } and { 3 } we have

$$\{1\} = 2\pi \Omega_1 J_0 \left(\Omega_1 \left[\bar{\omega}^2 - k^2\right]^{1/2} t \sin\theta\right) e^{-\Omega_1 kt}$$

(III.C. 20)

$$\{3\} = \Omega_2 \int_0^{2\pi} J_0(\Omega_3 t \sin\theta \cos\phi) J_0(\Omega_3 t \sin\theta \sin\phi) d\phi$$

(III.C. 21)

If we set $\Omega_2 = \Omega_1$ the remainder of the expressions (III.C. 18) and (III.C. 19) are identical. Using power series expansions for small time we find

$$\{1\} = 2\pi \Omega_1 [1 - \Omega_1 kt + \left(\frac{\Omega_1 kt}{2}\right)^2 - \frac{(\bar{\omega}^2 - k^2)(\Omega_1 t \sin\theta)^2}{4} - \frac{(\Omega_1 kt)^3}{6}$$
$$+ \frac{(\bar{\omega}^2 - k^2)(\Omega_1 kt)(\Omega_1 t \sin\theta)^2}{4} + \frac{(\Omega_1 kt)^4}{24} - \frac{(\bar{\omega}^2 - k^2)(\Omega_1 kt)^2(\Omega_1 t \sin\theta)^2}{8} + \cdots]$$

$$\{3\} = 2\pi \Omega_2 [1 - \frac{(\Omega_3 t \sin\theta)^2}{4} + \frac{5}{4}\frac{(\Omega_3 t \sin\theta)^4}{64} - \cdots]$$

Now if we let K 0 , (III.C. 22) becomes

$$\{1\} = 2\pi \Omega_1 [1 - \frac{(\bar{\omega} \Omega_1 t \sin\theta)^2}{4} + \frac{(\bar{\omega} \Omega_1 t \sin\theta)^4}{64} - \cdots]$$

Since $\Omega_1 = \Omega_2$, if we identify $\bar{\omega} \Omega_1 \cong \Omega_3$, we find the two expressions in substantial agreement to the order of our approximations.

Thus we see that the model of Kinzer and Chambers represents a three dimensional crystal quite well in the case $K \ll 1$ and may well be less unwieldy for numerical manipulation than the three-dimensional model.

APPENDIX

Let us define the Laurent-Cauchy transform pair as

$$F(\rho, t) = L_c[h_n(t)] = \sum_{n=0}^{\infty} h_n(t)\, \rho^{-n}$$

$$h_n(t) = L_c^{-1}[F(\rho, t)] = \frac{1}{2\pi i} \int_C F(\rho, t)\, \rho^{n-1}\, d$$

where the functions $F(\rho, t)$ and $h_n(t)$ of a real variable are Laplace transformable. Without concerning ourselves with the general theory of this transform, let us derive the following four transform pairs, which are used extensively in this paper.

$$L_c[h_{n+1}(t)] = \rho F(\rho, t) - \rho\, h_o(t) \tag{1}$$

$$L_c[h_{n+2}(t)] = \rho^2 F(\rho, t) - \rho^2 h_o(t) - \rho\, h_1(t) \tag{2}$$

$$L_c[COSH(a_o n)] = \frac{\rho(\rho - COSH\, a_o)}{\rho^2 - 2\rho\, COSH\, a_o + 1} \tag{3}$$

$$L_c[SINH(a_o n)] = \frac{\rho\, SINH\, a_o}{\rho^2 - 2\rho\, COSH\, a_o + 1} \tag{4}$$

For transform (1), we have by definition

$$L_c[h_{n+1}] = \sum_{n=0}^{\infty} h_{n+1}\, \rho^{-n}$$

$$= \rho\left[\sum_{n=0}^{\infty} h_{n+1}\, \rho^{-n-1}\right] = \rho\left[\sum_{n=1}^{\infty} h_n\, \rho^{-n}\right]$$

$$= \rho\left[\sum_{n=0}^{\infty} h_n\, \rho^{-n} - h_o\right] = \rho\left[L_c(h_n) - h_o\right]$$

$$= \rho\, F(\rho) - \rho\, h_c$$

Iterating the above result once, we obtain transform (2)

$$L_c \left[h_{n+2} \right] = L_c \left[h_{(n+1)+1} \right]$$

$$= p L_c \left[h_{n+1} \right] - p h_1 = p \left[p F(p) - p h_o \right] - p h_1$$

$$= p^2 F(p) - p^2 h_o - p h_1$$

Similarly, by definition, we have for transform (3)

$$L_c \left[COSH (a_o n) \right] = \sum_{n=0}^{\infty} \frac{1}{2} \left[e^{a_o n} + e^{-a_o n} \right] p^{-n}$$

$$= \frac{1}{2} \left\{ \sum_{n=0}^{\infty} \left(\frac{e^{a_o}}{p} \right)^n + \sum_{n=0}^{\infty} \left(\frac{e^{-a_o}}{p} \right)^n \right\}$$

Or, using the well known summation

$$\sum_{n=0}^{\infty} X^n = \frac{1}{1-X} , \quad |X| < 1$$

we have

$$L_c \left[COSH (a_o n) \right] = \frac{1}{2} \left[\frac{1}{1 - \frac{e^{a_o}}{p}} + \frac{1}{1 - \frac{e^{-a_o}}{p}} \right]$$

$$= \frac{p}{2} \left\{ \frac{2p - (e^{a_o} + e^{-a_o})}{p^2 - (e^{a_o} + e^{-a_o}) p + 1} \right\} = \frac{p(p - COSH \, a_o)}{p^2 - 2 p COSH \, a_o + 1}$$

Finally we have for transform (4)

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$$L_c\left[COSH\ (a_o n)\right] = \sum_{n=0}^{\infty}\ \frac{1}{2}\left[e^{a_o n} - e^{-a_o n}\right]\rho^{-n}$$

$$= \frac{1}{2}\left\{\sum_{n=0}^{\infty}\left(\frac{e^{a_o}}{\rho}\right)^n - \sum_{n=0}^{\infty}\left(\frac{e^{-a_o}}{\rho}\right)^n\right\}$$

Or, using the same summation as above, we obtain

$$L_c\left[SINH\ (a_o n)\right] = \frac{1}{2}\left[\frac{1}{1 - \dfrac{e^{a_o}}{\rho}} - \frac{1}{1 - \dfrac{e^{-a_o}}{\rho}}\right]$$

$$= \frac{\rho}{2}\left\{\frac{e^{a_o} - e^{-a_o}}{\rho^2 - (e^{a_o} + e^{-a_o})\rho + 1}\right\}$$

$$= \frac{\rho\ SINH\ a_o}{\rho^2 - 2\rho\ COSH\ a_o + 1}$$

The major development of the Laurent-Cauchy transform has been presented by Y. H. Ku and A. A. Wolf, Proc. Inst. Radio Engrs. 48, 923 (1960). An extensive table of Laurent-Cauchy transform pairs is also given in this article. A correction to this article has been presented by Y. H. Ku and A. A. Wolf, Proc. Inst. Radio Engrs. 49, 1097 (1961). Additional development of a related type of transform has been presented by E. I. Jury, J. Franklin Inst. 270 114 (1960).
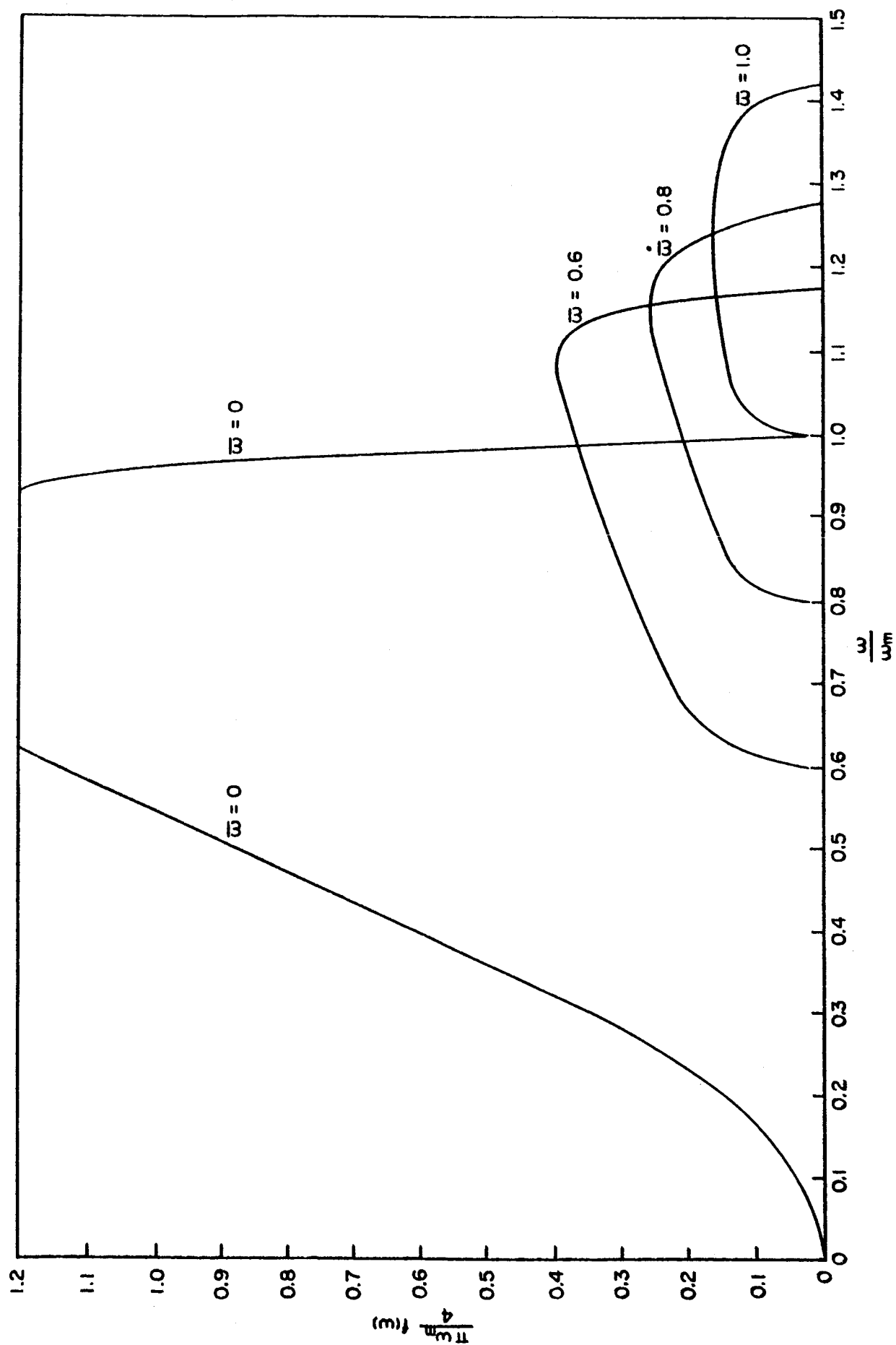
Fig. 1. Dependence of binding energy term on $\bar{w}$. ($K_E = 0$, $Z = 0.5$)
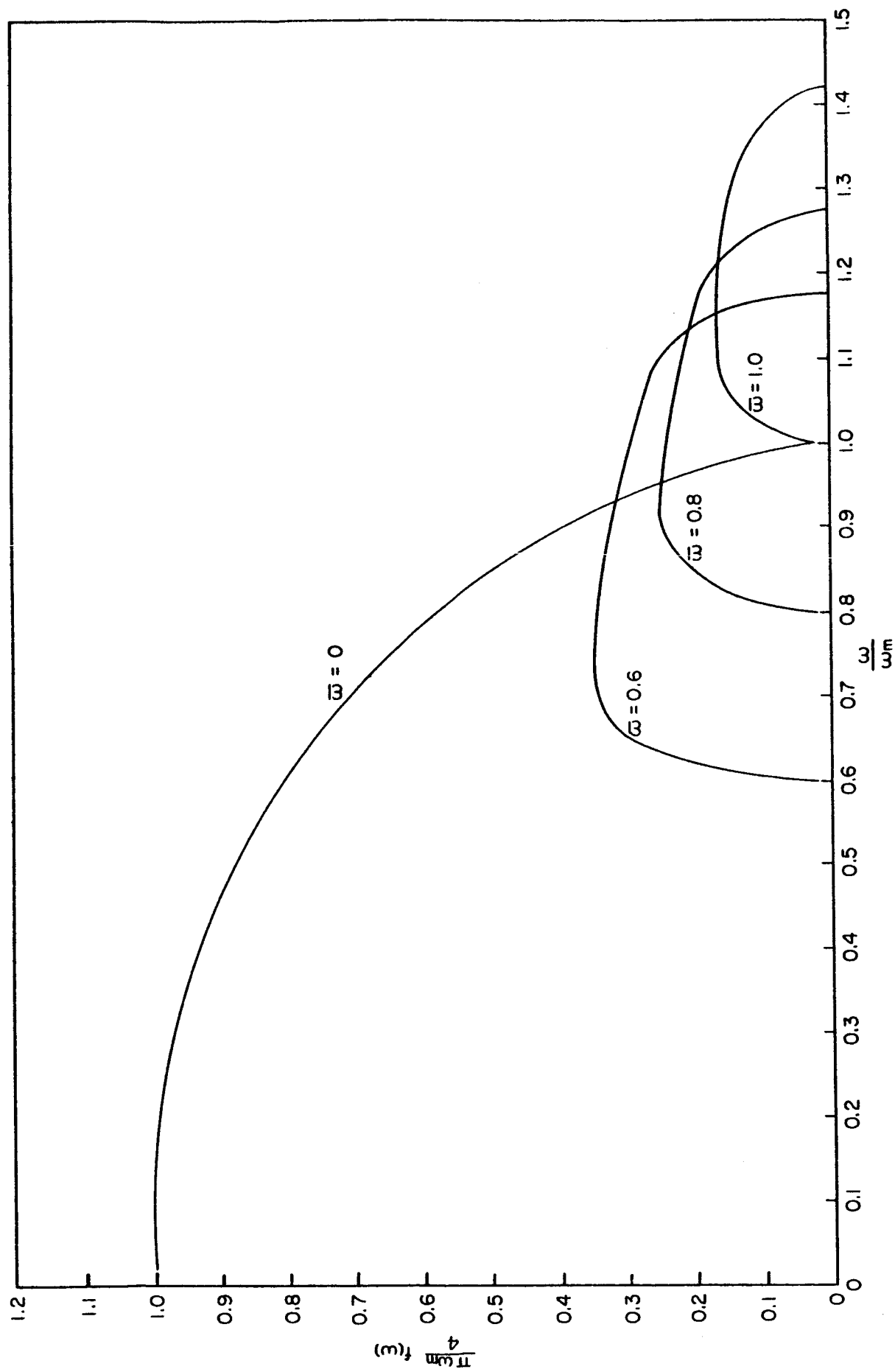
Fig. 2. Dependence of kinetic energy term on $\overline{w}$. (e = 0, Z = 0.5)
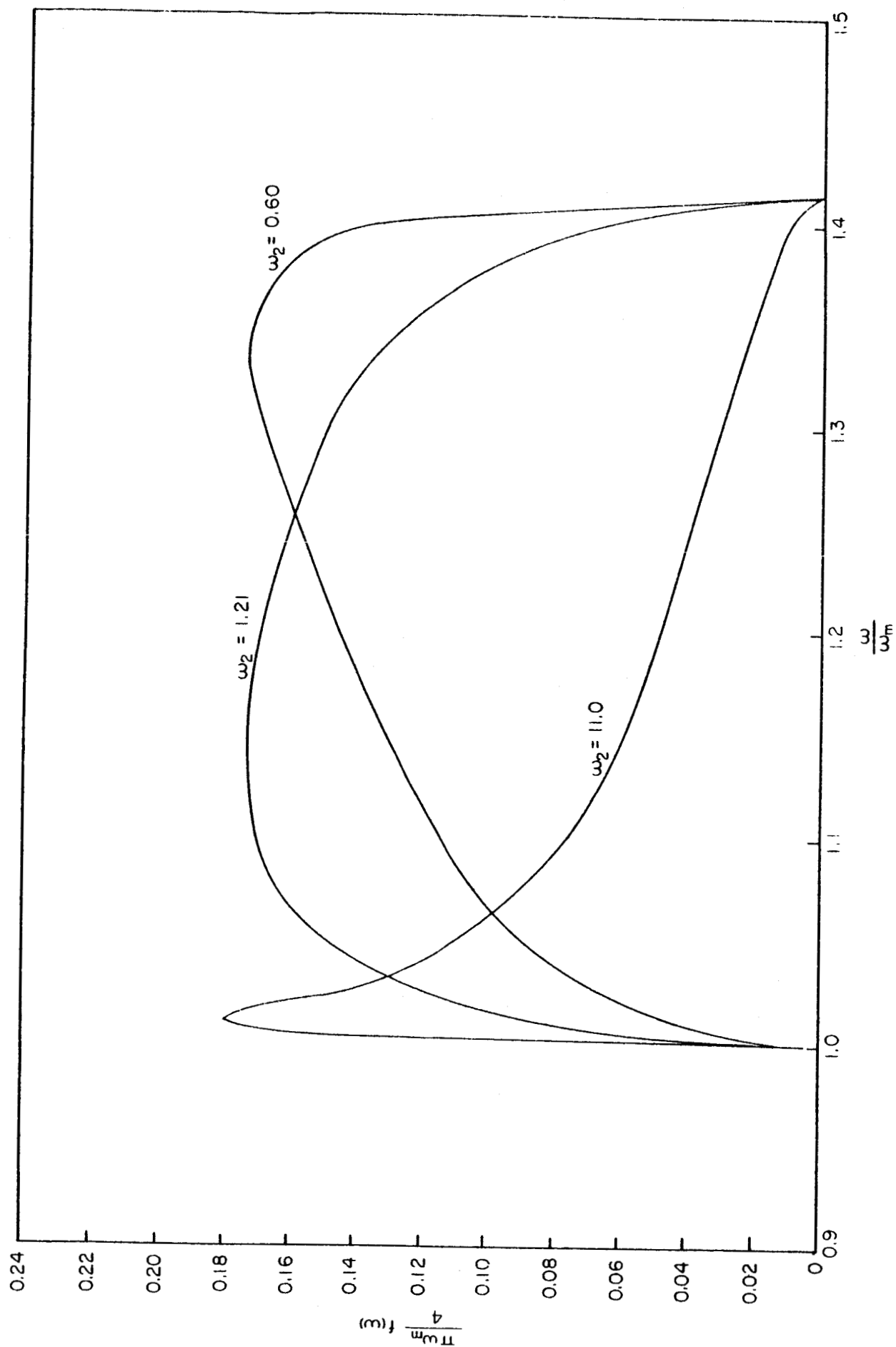
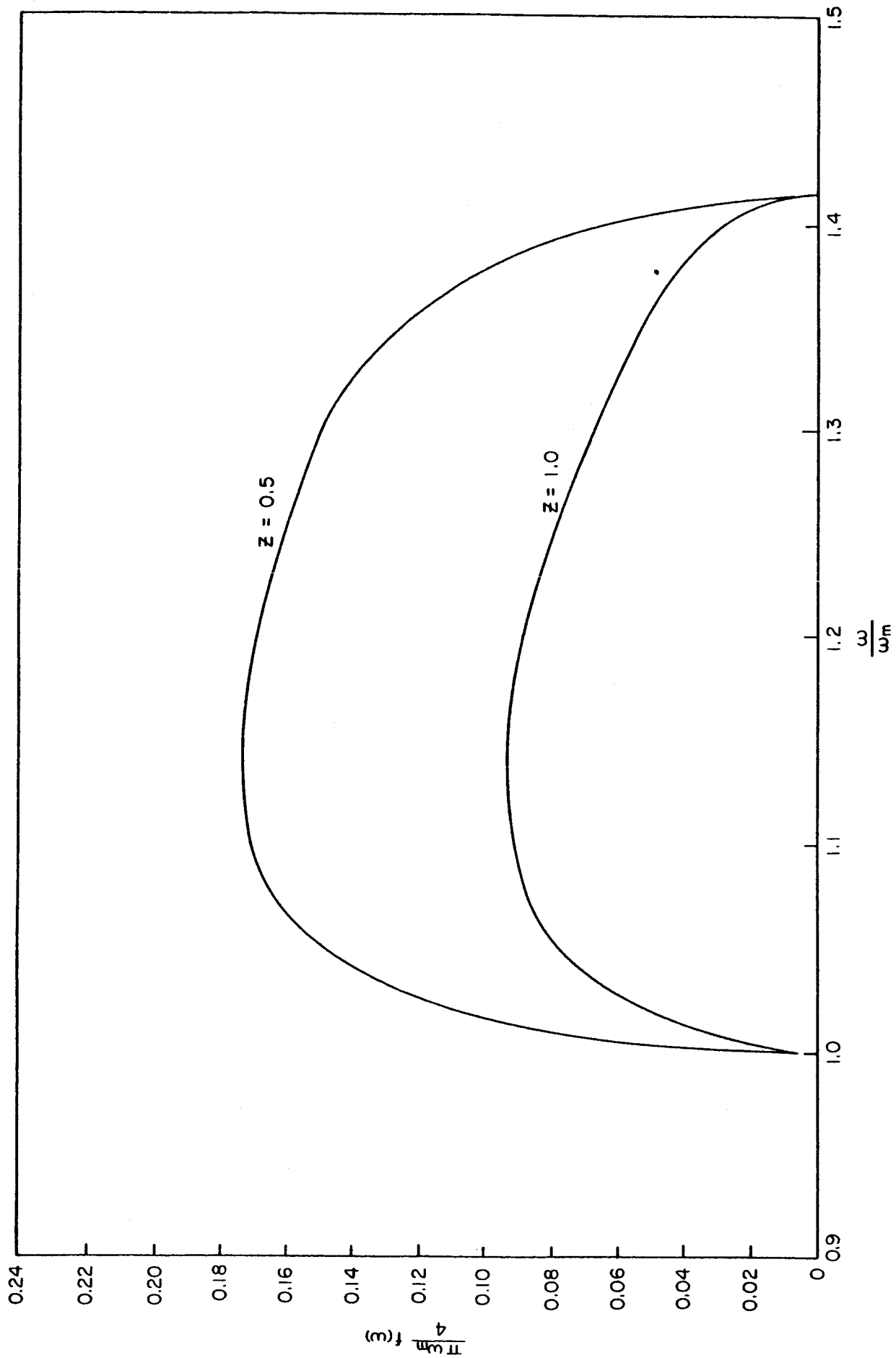Fig. 3. Dependence of kinetic energy term on w_2. ($e = 0$, $Z = 0.5$, $\overline{w} = 1.0$)

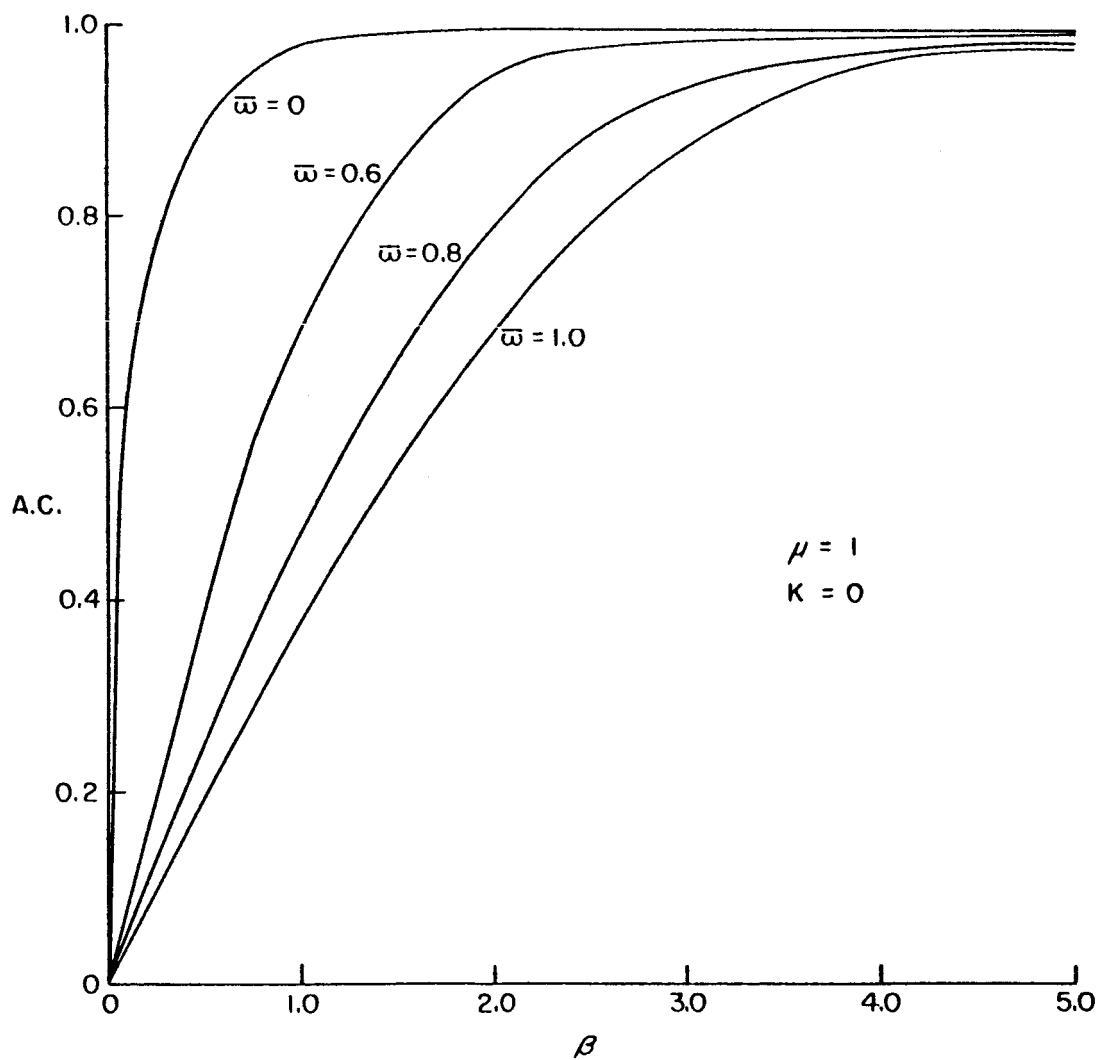Fig. 4. Dependence of kinetic energy term on Z. (e = 0, $\overline{w}$ = 1.0, w_2 = 1.21)
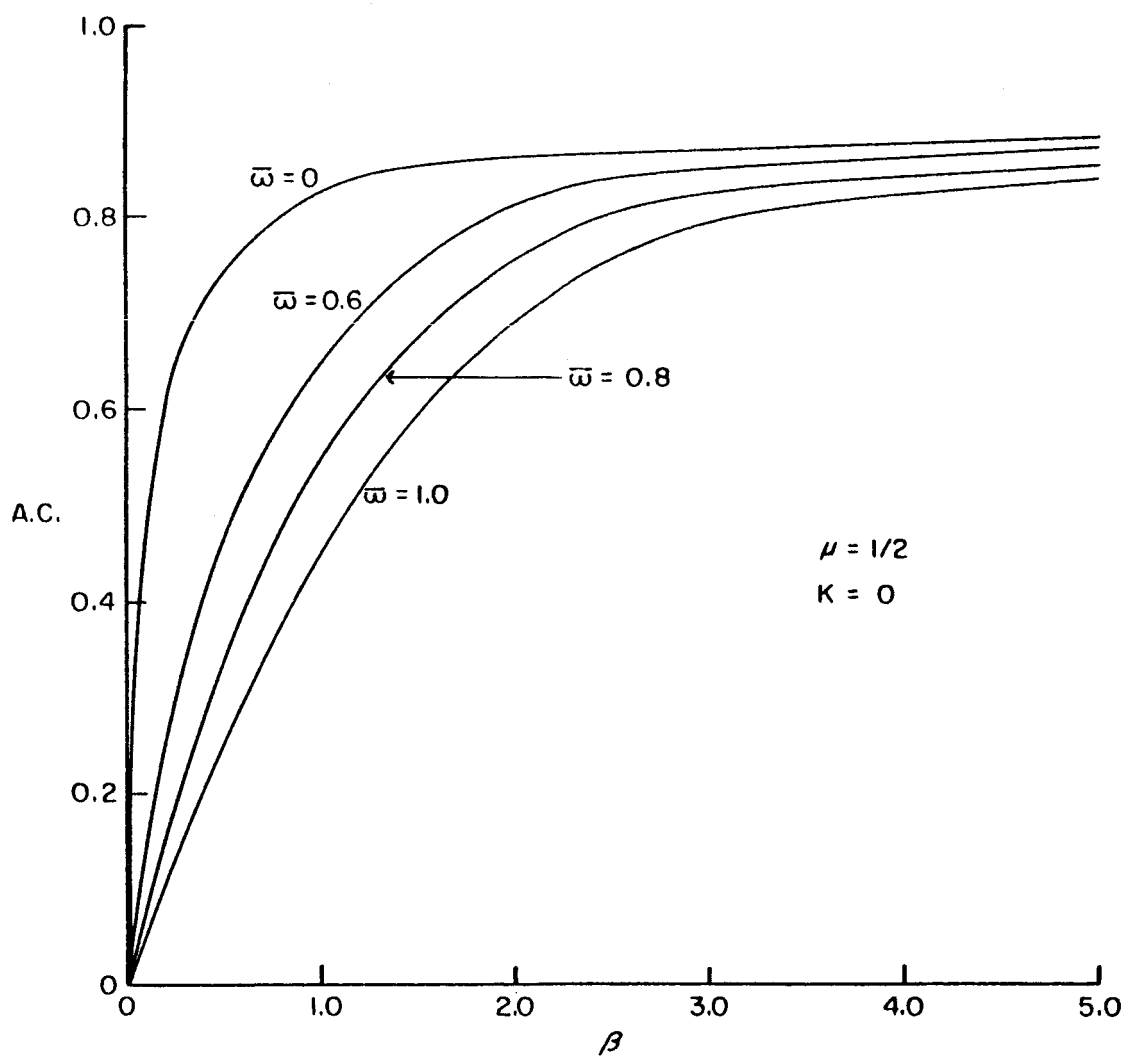
Fig. 5.   Dependence of accommodation coefficient on $\overline{w}$.
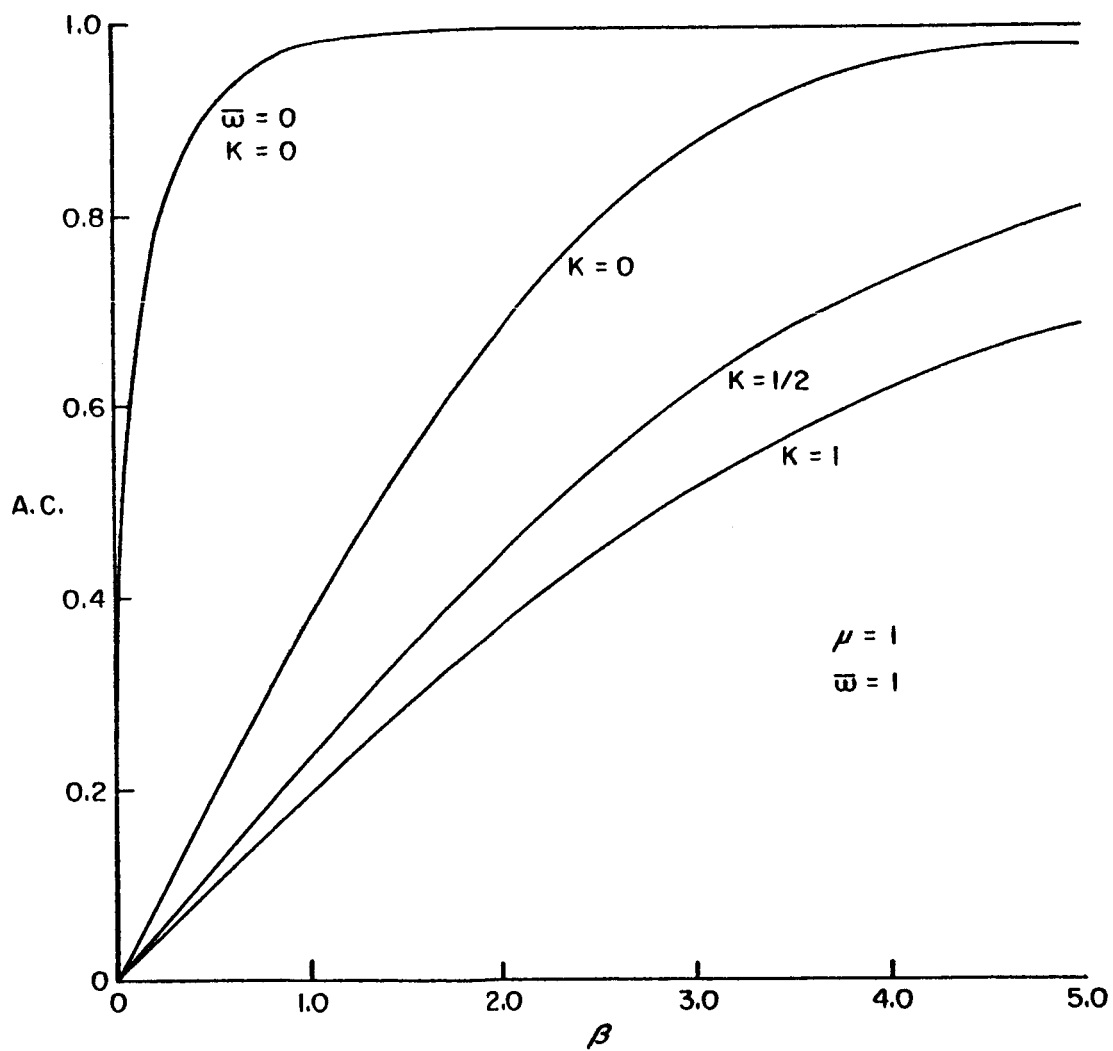
Fig. 6. Dependence of accommodation coefficient on $\overline{w}$.

Fig. 7. Dependence of accommodation coefficient on K.
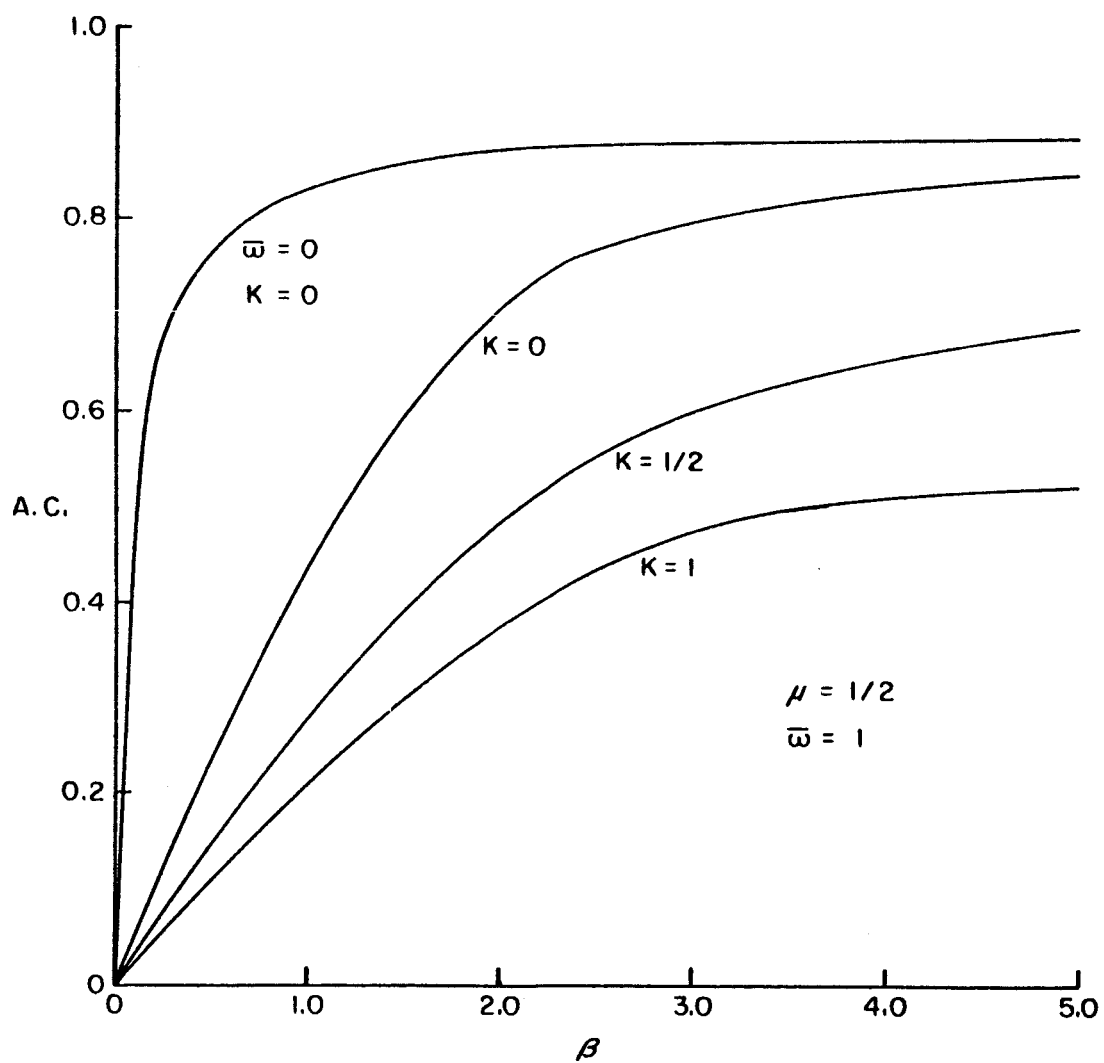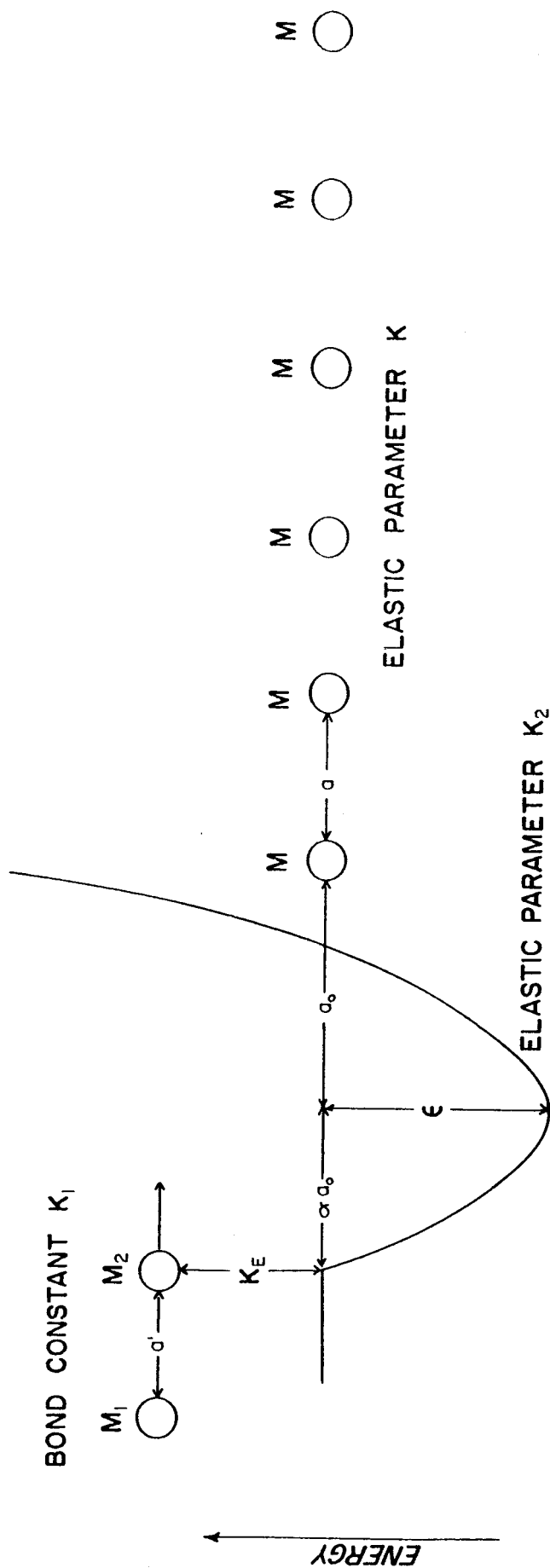
Fig. 8. Dependence of accommodation coefficient on K.
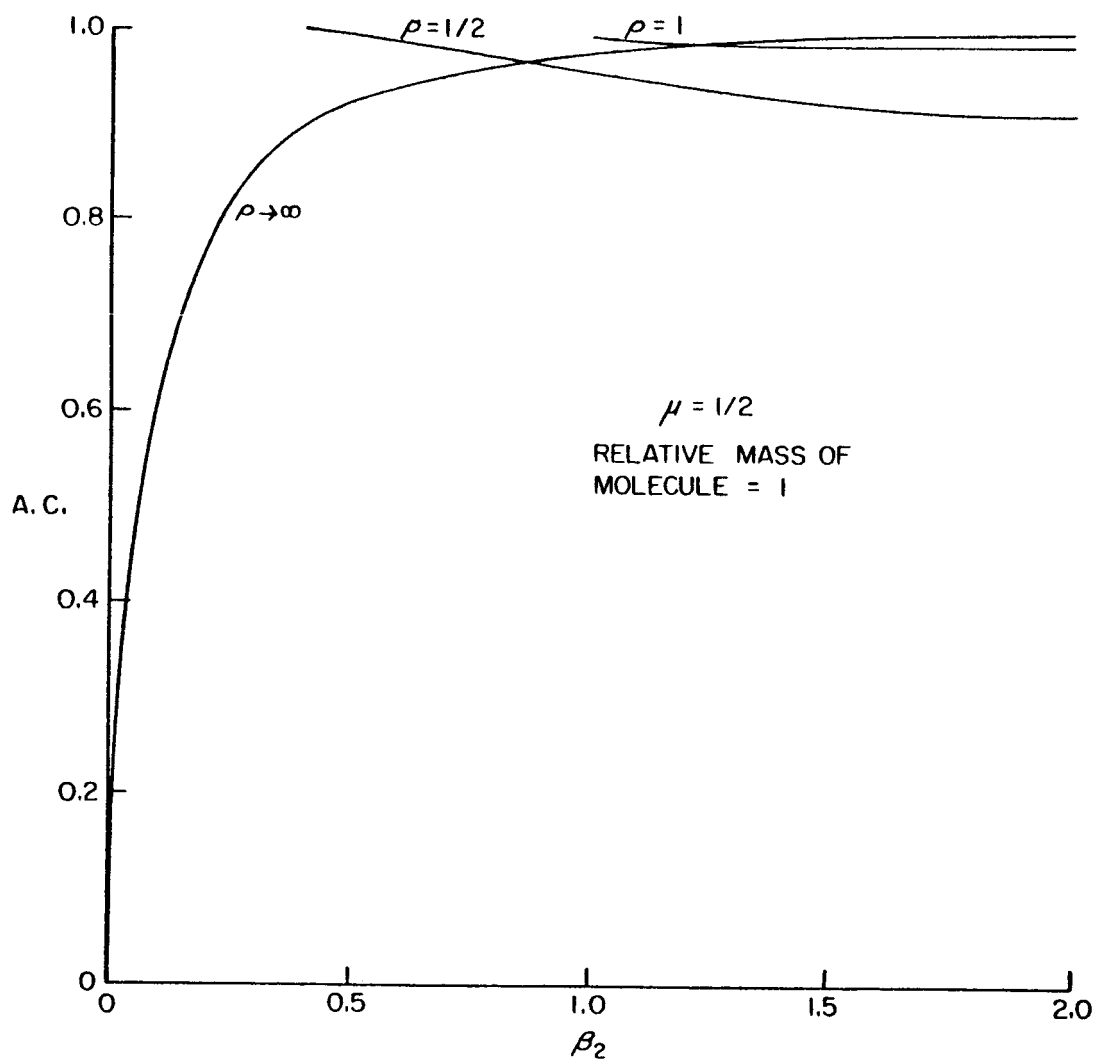
Fig. 9. Sketch illustrating diatomic molecule interaction.

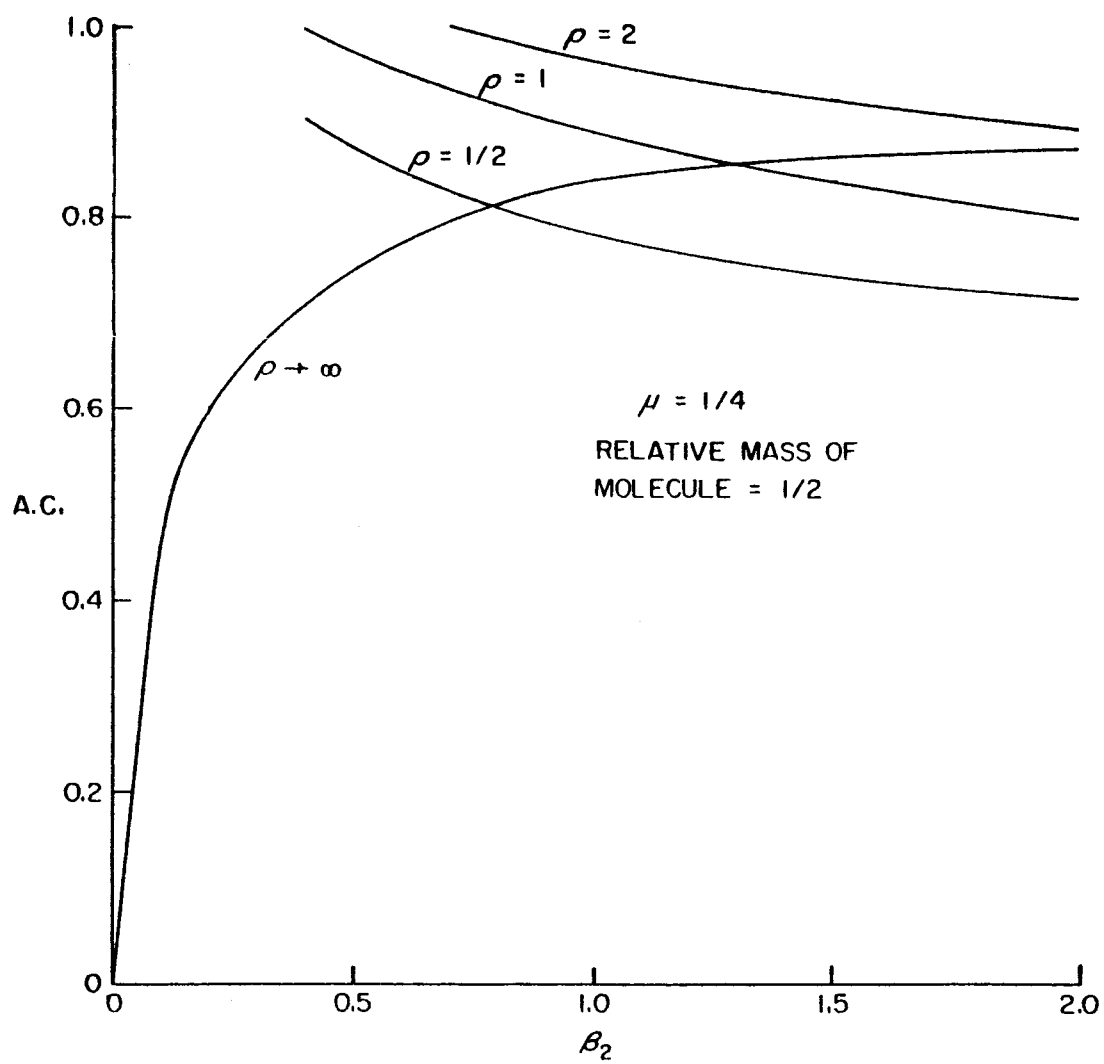Fig. 10. Dependence of diatomic accommodation coefficient on rho.

Fig. 11. Dependence of diatomic accommodation coefficient on rho.

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